

THE REVERSE MARTENSITE TRANSFORMATION

IN CERTAIN STAINLESS STEELS

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ABSTRACT

The reverse martensite transformation in three stainless steel alloys has been investigated; one was a pure ternary alloy (Fe - 16%Cr - 12%Ni), one also contained molybdenum and carbon (Fe - 15%Cr - 8½%Ni - 2%Mo - 0.1%C), and the other contained copper (Fe - 16%Cr - 10% Ni - 2%Cu). Each alloy was fully austenitic at room temperature after solution - treatment, but underwent partial transformation to martensite when quenched to -196°C or deformed at room temperature. The transformation was studied using room temperature measurements of specific saturation magnetic intensity, differential dilatometry, mechanical property measurements, and optical and electron microscopy.

The transformation of martensite during isothermal holding at temperatures between the A_S and A_f , and below the A_S , was found to involve the formation of a stable, low-nickel ferrite by a diffusional process. Suggestions have been made as to the reason for the formation of this ferrite, which could not be produced from initially austenitic specimens.

The effect of repeated transformation cycling has been studied and it was concluded that each generation of martensite nucleates mainly in the same areas as the first generation martensite; however, ^(successive generations) they may form only in the regions of ϵ , stacking faults and twins, lying between previous generation martensite crystals. The strengthening mechanisms of martensite and reversed

austenite have been investigated for quench-induced and deformation-induced martensite. The results suggest that the major strengthening mechanism of reversed austenite is its high dislocation density, but a different work hardening mechanism is involved in martensitic specimens due to the different crystal structures of martensite and austenite.

The reversion of deformation-induced martensite has been studied, together with the annealing of the reversed structures. The results indicate that reversed austenite probably inherits defects from the martensite. Reversed austenite was found to recover more rapidly but to recrystallise more slowly than retained austenite. Different recrystallisation mechanisms are suggested for the reversed and retained austenite.

The precipitation of copper before and after reversion has been studied. Precipitation was found to be rapid in martensite, but the precipitates were found to redissolve on reversion. Therefore, the copper-containing alloy was not found to be very useful in the study of reversion.

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INTRODUCTION

The austenite produced by reversion of martensite to austenite has been found, in several alloy systems, to be stronger than the original, annealed austenite. In stainless steels, 16% reversed austenite has been shown⁽¹⁾ to increase the strength of annealed austenite by over 50%. This strengthening effect has potential uses in that no shape change is necessary to increase the strength. Also, since reversed austenite has been found to have a fairly high ductility, reversion of deformation-induced martensite could be used to increase the ductility of deformed material to allow further deformation. Most of the investigations of reversion in iron-base alloys have been in the iron-nickel system; therefore, a general study of the transformation in stainless steels, which differ from iron-nickel alloys in their lower stacking fault energy, and in the morphology of their martensite phase, seems justified.

An initial investigation in this department by H. Smith⁽¹⁾, using two stainless steels, showed the reversed austenite to be in the form of heavily dislocated laths. Smith investigated the effect of carbide precipitation after reversion and also the annealing behaviour of reversed austenite. The aim of the present project was to extend the work of Smith to investigate the isothermal transformation of martensite to austenite between the A_s and A_f ; to examine the sites in which second generation martensite formed after reversion and, thus, the stabilisation

of austenite resulting from reversion; to investigate the strengthening mechanisms leading to the enhanced strength of reversed austenite; to observe the effect of reversion on deformation-induced martensite; and to extend Smith's work on carbide precipitation to other precipitates.

Three alloys were used in the experiments. Two were duplicates of those used by Smith. Firstly, a pure iron-chromium-nickel ternary alloy, alloy A, was used, in which the reverse transformation could be studied without any possible decomposition of the martensite involving precipitation during heating. Secondly, an alloy, alloy B, containing molybdenum and carbon was used in order to allow the possibility of carbide precipitation and to investigate the general effect of carbon on the strengthening obtained. Thirdly, an alloy, alloy C, containing copper was used, in order to allow the possibility of precipitation (of basically pure copper) without drastically changing the matrix composition and thus the M_s . The compositions of these alloys were balanced so that solution treatment could produce a fully austenitic structure which was retained, by fast cooling, at room temperature.

The compositions also had to be balanced so that the M_s was sufficiently below room temperature to allow room temperature measurements without the possibility of second generation martensite, but high enough to allow a reasonable amount of martensite to be produced by quenching to -196°C . In the case of alloy C the copper content was kept low enough for the M_s to remain below room temperature even

after precipitation. The compositions chosen were:

alloy A, Fe - 16wt% Cr - 12wt% Ni; alloy B, Fe - 15wt% Cr - 8.5wt% Ni - 2wt% Mo - 0.09wt% C; alloy C, Fe - 16wt% Cr - 10wt% Ni - 2wt% Cu.

CHAPTER 1.

REVIEW OF LITERATURE

1.1 General

There is a vast amount of literature in existence relating to martensitic transformations in steels, and much of the work on the direct transformation in stainless steels, and the reverse transformation in various systems, is relevant here. A fairly comprehensive review of the literature was made in 1968 by H. Smith⁽¹⁾; therefore, only the most important points dealt with by him will be mentioned here, whilst concentrating on work relating to the mechanism of reversion in stainless steels, transformation cycling and aspects of strengthening by reversion.

1.2 The Direct Transformation to Martensite in Stainless Steels

a) The effect of composition

Much of the early work on stainless steels was concerned with the variation of the M_s temperature with composition. Generally it was found that all alloy additions depressed the M_s ⁽²⁻⁵⁾, the effect being particularly sensitive to the carbon content^(2,3,6). Attempts to derive an empirical formula relating the M_s to composition^(2,3) were not very successful.

The morphology of the martensite has also been found to vary with alloy composition^(7,8). Breedis⁽⁸⁾ found 3 types of martensite with varying Cr and Ni contents in an

Fe-Cr-Ni alloy. If Cr + Ni was less than 26 weight percent he found a lath morphology. If Cr + Ni was greater than 26 weight percent, then surface and plate martensites began to appear. Kelly and Nutting⁽⁷⁾ found a lath morphology in a low-carbon, 18/8 stainless steel, and internally twinned plates in higher carbon stainless steel and in Fe-Ni alloys. Thus, in the alloys used in this project, lath martensite is expected and therefore we will concentrate on the literature relating to that type.

Kelly and Nutting⁽⁷⁾ found the martensite in an 18/8 stainless steel to consist of needles oriented with their long axis parallel to $\langle 1\bar{1}0 \rangle_{\gamma}$. The needles were collected in sheets on the $\{111\}_{\gamma}$ planes, with the sets of needles within a sheet always being twin related. Very similar results were obtained by Breedis for 19/11, 17/11, 16/12 and 13/14, Cr/Ni, Stainless steels.

(b) Nucleation.

An h.c.p. phase, ϵ , has been found by many workers^(8-25,68) in Fe-Cr-Ni alloys with low stacking fault energy. Generally, for the S.F.E. to be low enough, Cr + Ni needs to be greater than about 26 wt.% (20)

There has been considerable discussion as to whether or not ϵ is an intermediate phase in the transformation of austenite (γ) to martensite (α'). The suggested transformation sequence is $\gamma \rightarrow \text{S.F.'s} \rightarrow \epsilon \rightarrow \alpha'$. This is supported by the fact that many workers (11,12,14,16-18,68) have found α' to be always associated with ϵ , at least in lath martensites. Other workers^(8,13,21), however, have found that, although

α' is usually associated with ϵ , it can occur without ϵ . The nucleation of α' on ϵ has been observed optically by Reed⁽¹¹⁾ in an 18/8 stainless steel, and Sanderson⁽²⁶⁾ in a Cr-Mn steel. Generally α' has been found to nucleate at the intersections of ϵ sheets^(11,26,68). Breedis⁽⁸⁾ found that the α' often had irregular interfaces where it was bounded by ϵ and faulted γ ; when he increased the nickel and decreased the chromium in the alloy to eliminate the ϵ and stacking faults, the regions between α' crystals then contained a high density of perfect dislocations.

If ϵ were an intermediate phase, it would need to appear before the α' ; therefore there should be both an M_s for α' and an M_s for ϵ . Goldman et al⁽²⁴⁾ failed to detect two M_s temperatures using three sensitive techniques; however, other investigators^(14,18,68) have found ϵ to appear before any α' was detected. Mangonon and Thomas⁽⁶⁸⁾ point out that it is very difficult to measure M_s temperatures using thermal analysis as attempted by Goldman et al⁽²⁴⁾.

It has been suggested⁽⁸⁻¹⁰⁾ that the ϵ is not a stable h.c.p. phase, but arises from intrinsic deformation faults being introduced into the γ , as a result of the strains accompanying the martensitic transformation. Mangonon and Thomas⁽⁶⁸⁾ refute this argument firstly because they found ϵ present before any martensite formed, and secondly because they found some ϵ within two martensite grains, with the martensite growing and consuming the ϵ . They state that martensite nucleates at the intersections of two ϵ plates, or of an ϵ plate with a twin or grain boundary, i.e. at regions under a compressive stress.

Dash and Otte⁽¹³⁾ decided that ϵ was not an intermediate

phase since the width of the ϵ plates depended on the size, shape and distribution of α' . Also, they found that it was possible to suppress the ϵ , but not the α' , by deformation. They did not, however, preclude the possibility of ϵ regions acting as nucleation sites for α' .

Generally, it has been found that small strains due to deformation applied above the M_d , increase the ϵ content of steels, whereas large strains decrease it. Deformation has a similar effect on the subsequent formation of α' on cooling to -196°C . Lagneborg⁽¹⁴⁾ found that small strains applied above M_d increased the α' content on cooling, but had little effect on the M_s , indicating an increase in the number of nuclei but not in their size. Kelly and Nutting⁽⁷⁾ suggest that small deformations produce wide stacking faults, which are effective nuclei for α' , whereas large deformations produce more, but narrower, stacking faults, which are less effective nuclei.

c) The effect of deformation

It has been shown^(15,27,68) that martensite can be induced along active slip planes in austenitic stainless steels by deformation of austenite above the M_s temperature. Also, below the M_s temperature, transformation to martensite is enhanced by deformation. Fielder et al⁽²⁷⁾ showed that the number, but not the width, of α' plates was increased by deformation, implying that the number of nucleation sites was increased.

Several workers^(7,11,14,27,28) have found that small deformations of the austenite enhance subsequent transformation

to α' , whereas large deformations retard it. Breedis⁽²⁸⁾ suggests that the reason for this is that after small deformations, dislocation pile-ups are produced since the dislocations are restricted to the slip planes. These pile-ups give rise to long range stress fields which can act as nucleating sites for α' . Large deformations, however, result in the formation of a cell structure due to cross-slip, and thus the long range stress fields are easily relaxed. More heavily deformed austenite also offers more resistance to transformation strains.

Brienan and Ansell⁽⁶⁹⁾ found the M_s of various medium alloy steels to decrease linearly with increasing flow stress of both deformed and undeformed austenite. The amount of α' formed at a given temperature was also less for stronger austenites. They concluded that the M_s was affected by either the ease of nucleation or the ease of growth of α' plates.

Other workers^(7,14,27,68) have suggested that the transformation is stimulated by small deformations because of the generation of wide stacking faults and ϵ phase which act as nuclei.

d) Isothermal transformation

Martensite has been shown to form isothermally both below, and just above, the M_s ; in fact some workers^(14,23,25) have found a C-curve behaviour with decreasing temperature. Lagneborg⁽¹⁴⁾ found the nose of the C - curve for an 18/8 stainless steel to be -150°C . Imai⁽²³⁾, however, found two noses for a 17/8 stainless steel. one at -100°C and the other at -135°C . Microstructurally he found γ , ϵ and α'

at the upper nose, and only γ and α' at the lower nose. On reducing the nickel content of the steel to eliminate ϵ he found that only one nose appeared. He concluded, therefore, that ϵ formed isothermally at the upper nose and α' then nucleated upon it.

Kulin and Speich⁽²⁵⁾ found the shape of the nucleation curve for isothermal α' to be similar to that for a normal nucleation and growth process.

Breedis and Robertson⁽¹⁵⁾ found that, for a 16/12 stainless steel, no isothermal transformation occurred at room temperature unless there was some α' present from a previous athermal transformation.

Reed and Mikesell⁽⁵⁾ suggest that the isothermal transformation is due to strained regions around previously formed α' laths providing nucleation sites which are then activated by thermal fluctuations.

The isothermal transformation has been shown to begin rapidly and then slow down with time.⁽²⁵⁾

e) Theories on the mechanism of transformation.

Kelly and Nutting⁽⁷⁾ suggest that the formation of needles is not explained by conventional theories for the formation of plate martensite because there appears to be an invariant line rather than an invariant plane as is found with plates. They proposed a modification of the Kurdjumov-Sachs relationship⁽⁷⁰⁾, to take this into account, and suggested that ϵ is an intermediate phase nucleating α' at the junction of two intersecting faults.

In a later paper⁽¹²⁾ Kelly suggested that the experimental

results could be predicted by the Bowles-Mackenzie⁽⁷¹⁾ theory using a $(111)_{\gamma} [\bar{1}2\bar{1}]_{\gamma}$ lattice invariant shear with a dilation parameter of 1.0185. He then suggested that laths are formed because the growth of plates is restricted by the width of the ε bands.

Lagneborg⁽¹⁴⁾ suggests that, since the structure in the centre of a Shockley partial is b.c.t. for about 2 atom layers and in wide stacking faults there are wide sheets of this structure, these stacking faults provide favourable sites for the nucleation of α' . These α' embryos then grow to form stable α' with the aid of slip processes in the γ during the preceding deformation. This is consistent with the formation of α' as needles along intersections between ε discs.

Venables⁽¹⁸⁾ suggests that α' nucleates on ε and then grows by the motion of parallel screw dislocations. In support of this Koepke⁽²⁹⁾ showed the γ/α' interface to be a parallel grid of dislocations which appeared to lie along the intersection of $(11\bar{1})_{\gamma}$ fault planes and $(1\bar{1}1)_{\gamma}$ habit planes. He, however, suggests that, when propagation of the interface ceased and the stress holding the dislocations together relaxed, it allowed them to split into two Shockley partials, one of which then glided into the γ and thus this was how the stacking faults formed.

Mangoni and Thomas⁽⁶⁸⁾ state that nucleation of α' is characterised by a region of compressive stress, that is at the intersection of ε plates or at the intersection of an ε plate with a twin or grain boundary. They then suggest that, since the pressure is not hydrostatic, it can be

relieved by an expansion to the b.c.c. lattice as, for the same force, a larger volume experiences less pressure per unit area. They observed the Nishiyama relationship between γ and α' in the early stages of transformation and propose that ϵ can transform to α' in essentially the Nishiyama relationship with γ , by the movement of partials in the $\{111\}_{\gamma}$ planes, which is equivalent to the system $\{110\}\langle\bar{1}10\rangle_{\alpha}$ in the b.c.c. structure. Then, in order to get the actual b.c.c. structure a compressive stress is needed along $\langle 211 \rangle_{\gamma}$ and $\langle 111 \rangle_{\gamma}$ directions. The greatest stress is needed in the $\langle 211 \rangle_{\gamma}$ and this is provided at the ϵ intersections mentioned above.

In a recent review Breedis and Kaufman⁽⁷³⁾ estimated the free-energy differences between α , ϵ and γ for a number of steels using the regular solution approach. They concluded that it is possible to form ϵ , in several Fe-Cr-Ni alloys, by quenching, where it is not thermodynamically stable with respect to γ and therefore spontaneous transformation of γ to ϵ is not expected. However, it is possible to produce stress-induced ϵ by the prior formation of α' . Therefore the ϵ is a form of accommodation deformation, as are deformation twins and the high dislocation density. They conceded, however, that ϵ may assist in subsequent nucleation of α' . They stated that the γ to α' transformation is thermodynamically possible and there is therefore no necessity for an intermediate ϵ phase.

In dealing with the morphology and crystallography of the transformation to lath martensite Breedis and Kaufman found that although Kelly's theory closely predicted the

habit plane, it did not explain the observed deviation of the long direction of the laths from $\langle 110 \rangle_\gamma$, which means that the habit plane must be irrational, and therefore cannot be the $\{112\}_\gamma$ predicted by Kelly. Also, recent shape strain measurements by Dunne and Bowles⁽⁷⁴⁾ have shown the dilatation parameter to be unity. In view of this Breedis and Kaufman concluded that the present phenomenological theories are unable to predict the observed habit plane in steels where the direction cosines deviate from near $\{135\}_\gamma$. Bowles and Dunne avoided this difficulty by introducing a lattice invariant accommodation strain into the earlier theory, but this approach has not yet been applied to describe irrational habit planes. The activation of multiple slip systems is evident within transformation bands for cases where undissociated dislocations are observed between α' laths, and this also must be incorporated into the theory.

1.3 The Reverse Martensite Transformation

a) Occurrence and Structural Aspects

Early work by Uhlig⁽³⁰⁾, and Wasserman⁽³¹⁾ suggested the martensitic, rather than diffusional, nature of the transformation of martensite to austenite under rapid heating conditions; this conclusion was reached because the transformation occurred as a function of temperature rather than time. Further work has confirmed the occurrence of a shear mechanism by the observation of surface tilting produced by the transformation. Both martensite and ferrite have been found to transform martensitically to austenite, under sufficiently rapid heating, in a number of alloy systems, including pure iron⁽³²⁾, iron-nickel^(33-57,75) and stainless steels^(1,4,11,16,17,58,59). The literature on most of the alloy systems has been covered by Smith⁽¹⁾ in his review and therefore only those particularly relevant to this project will be covered here. A number of workers have used reversion in order to refine the austenite grain size of steels; this aspect has been adequately reviewed by Grange⁽⁷⁶⁾ and will not particularly be discussed here.

In stainless steels of composition approximately Fe-16Cr-12Ni ϵ has been found^(1,11,17) to revert to γ at approximately 400°C, and martensite to revert at 500-600°C. After reversion the areas previously occupied by martensite are dark etching and can be seen under the optical microscope; they have been termed 'Ghost areas'.

In stainless steel the orientation of the original austenite grain has been found^(1,58) to be reproduced by

reversion, although small twins and deformation faults are present in the regions of reversed austenite. The fine structure of the reversed austenite consists of a high and varied density of complex dislocation tangles, most of which are thought to be inherited from the martensite. In stainless steels in which lath martensite is produced, there is no substantial deformation of the austenite outside the transformation band⁽¹⁾; however, with the plate martensite in iron-nickel alloys there is deformation of the retained austenite.⁽⁷⁵⁾

Nagpaul and West⁽⁷⁵⁾ found, in an Fe-Ni-C alloy, that some areas of reversed austenite contained a banded structure in which the bands were twin-related, and ran across the plates of reversed austenite. They suggest the origin of the bands may have been the coalescence of twins from the martensite.

b) Mechanical Properties.

The limited amount of work which has been done on stainless steels indicates that the strength of reversed austenite is considerably greater than that of the annealed austenite from which it is obtained. Smith⁽¹⁾ found an increase in hardness of about 50% when 15% reversed austenite was introduced into the annealed austenite of a Fe-16Cr-12Ni alloy. Krauss⁽⁴⁵⁾ found the yield strength of an Fe-33.5 Ni alloy, to be doubled by 60% reversed austenite, the dislocation density in the reversed austenite being about ten times that in the retained austenite. Greater strength increases have been obtained by producing reversed austenite

in iron-nickel alloys than in stainless steels, but this seems to be mainly due to the higher percentages of α' which can be obtained in Fe-Ni alloys. It is difficult to make a comparison, of the strength increase per percentage reversed austenite, for Fe-Ni alloys and stainless steels, since nearly all of the measurements on Fe-Ni alloys have been for 70-100% reversed austenite, and such measurements as there have been for stainless steels were performed with 0-20% reversed austenite. The comparison is difficult since Gorbach and Malyshev⁽⁷⁷⁾ have shown that the relationship of yield stress with percentage reversed austenite, in Fe-Ni alloys, is non-linear. However, a comparison at 15% reversed austenite using the work of Gorbach and Malyshev⁽⁷⁷⁾ for Fe-Ni. and Smith⁽¹⁾ for Fe-Cr-Ni, indicates that the strengthening increment for Fe-Ni is less than that for Fe-Cr-Ni.

All workers have attributed the strength increase of reversed austenite as compared with annealed austenite, to the fragmentation and disorientation of the crystal lattice, and to the high dislocation density in reversed austenite.

The work hardening capacity and ductility of reversed austenite has been found to be less than that of annealed austenite⁽⁴⁶⁾.

Generally, the maximum strength is obtained when reversion is carried out for the minimum time at the minimum temperature above the A_f ; since, when either time or temperature is increased, recovery and recrystallisation begin and the strength drops, eventually

reaching that of annealed austenite. Ankara⁽⁷⁸⁾, however, found that, in an Fe-30% Ni alloy, due to the formation of a cell structure, the strength, under rapid heating, continued to increase with austenitising temperature for about 100°C above the A_f .

It has been found^(75,77) that the addition of carbon to Fe-Ni alloys, whilst affecting the overall strength, has very little effect on the strengthening achieved by reversion under rapid, short time austenitising conditions. Nagpaul and West⁽⁷⁵⁾ therefore concluded that the main strengthening was due to the high dislocation density. The same authors attributed the non-linear relationship of yield stress with percentage reversed austenite, to the deformation introduced into the retained austenite by the direct and reverse transformations.

c) Effect of Annealing.

The annealing of reversed austenite at temperatures above the A_f has been found to result in the gradual disappearance of the defect structure until a normal recrystallised austenite is obtained. Breedis⁽⁵⁹⁾ found that, in an 18/8 stainless steel, stress relief continued for about 24 hours at 600-800°C. Smith⁽¹⁾, in a 16/12 stainless steel, found that the annealing-out of defects in reversed austenite produced from quench-induced martensite, was a process of 'continuous recovery', not involving the movement of high angle boundaries. The final austenite grain size was thus the same as that of the original annealed austenite. However, in reversed austenite produced from cold worked

martensite he found true recrystallisation to occur involving the movement of high angle boundaries. He suggested that the mechanism of recovery in the quenched specimen was that of recrystallisation 'in situ', i.e. involving sub-grain coalescence. He also found some fine twins in areas of reversed austenite and suggested that they may have formed in the initial stages of recovery.

Izmailov et al⁽⁴⁰⁾ found that recrystallisation in an Fe-Ni alloy proceeded in two stages. Firstly, at a relatively low temperature, the reversed austenite recrystallised; then, at a higher temperature, the retained austenite recrystallised. Zaytsev and Gorbach⁽⁵⁷⁾, however, whilst agreeing that the reversed austenite recrystallised first, found that the retained austenite did not recrystallise separately, but that the recrystallised grains formed from the reversed austenite grew into the retained austenite regions.

Krauss and Cohen⁽⁴⁶⁾ found that, on heating their Fe-Ni alloy to about 50°C above the A_f , islands with clearly developed boundaries, though imperfect fine structure, appeared. They termed these islands 'reversal twins' and suggested that they were part of the recovery process. They postulated that these twins were formed by the coalescence of high energy stacking faults. At higher temperatures, they found that recrystallisation proceeded by the movement of the existing austenite boundaries sweeping out the fine structure, rather than the formation of new grains.

Nagpaul and West⁽⁷⁵⁾, using an Fe-Ni-C alloy, found that, at high temperatures, recrystallisation involved the nucleation

and growth of new grains, the final structure being recrystallised and having a somewhat finer grain size than the original. However, at lower temperatures, the final, softest structure was not found to be completely recrystallised, and it was assumed that recovery made a large contribution which involved the formation of a sub-grain structure.

Golovchiner⁽³⁴⁾ found that increasing the heating rate for reversion caused a lowering of the recrystallisation temperature, and an increase in the recrystallisation speed.

d) The Mechanism of the transformation.

It seems well established that, at sufficiently rapid heating rates, the $\alpha' \rightarrow \gamma$ transformation can occur martensitically. Even in single crystals of pure iron Zerkweh and Wayman⁽³²⁾ have shown that enough superheating can be obtained for the $\alpha \rightarrow \gamma$ transformation to proceed martensitically. The proof of the martensitic nature of the transformation was that surface tilts were generated.

As regards the transformation in stainless steels, Breedis⁽⁵⁹⁾ concluded that the reverse transformation substantially retraced the path of the direct, martensitic transformation, rather than occurring by a recrystallisation process. Similar results were obtained by Thomas and Krauss⁽⁵⁸⁾, and Smith⁽¹⁾, in that they found regions of reversed austenite with a high and varied density of dislocation tangles, amid relatively dislocation-free regions of retained austenite. Smith⁽¹⁾ showed that individual grains of α' retransform completely to austenite of the same orientation as the retained austenite, producing regions of reversed austenite of similar size and

shape to the original martensite grains.

Similar conclusions have been reached for rapid heating conditions with Fe-Ni alloys. Some early Russian work⁽⁶¹⁾ suggested that the surface tilting produced by the reverse transformation was a mirror reproduction of that produced by the direct transformation. Later work^(35,37,40,60), however, showed the position to be more complicated than this. Reversion has been found to begin at the periphery of the α' plates in Fe-Ni alloys, and Krauss and Cohen⁽⁴⁶⁾ then found the plates to break up in a piecewise fashion, leaving the original δ grain size, and annealing twins, unchanged. Gorbach and Butakova⁽³⁷⁾ found that each α' crystal transformed over a wide temperature range, small austenite platelets forming very quickly, and lying across and intersecting the α' crystal. The δ platelets ceased to grow in a very short time, and further transformation proceeded by the nucleation and rapid growth of new platelets. They suggest that the reason for this fragmentation is a reduction in the elasticity of the medium on heating, together with the substructure in the α' , hindering the growth of the δ crystal. Shapiro and Krauss⁽⁵²⁾ found no midrib after reversion and concluded that the transformation proceeded in one direction from the nucleation point.

Several Russian workers^(35,47) have concluded that the mosaic structure resulting from this fragmentation of the α' grains, is the reason for the δ stabilisation produced by reversion in both Fe-Ni and Fe-Cr-Ni alloys. Another suggestion⁽³⁷⁾ is that the stabilisation is a result

of severe distortion of the lattice by both the direct and reverse transformations. Golovchiner and Tyapkin⁽³⁵⁾ however, found that deformation of an Fe-Ni-Ti alloy did not result in γ stabilisation, whereas reversion did. They therefore attributed the stabilisation to fragmentation of the lattice. Maksimova and Nikonorova⁽⁴⁷⁾ reached the same conclusion when they found that restoration of the original γ stability did not occur until a temperature well above the recrystallisation temperature. Several workers^(37,40,55) have found that the reversed austenite inherits the block disorientation and defect structure of the α' from which it came.

Kessler and Pitsch⁽⁴⁴⁾ found that, for an Fe-32.5 Ni alloy, the orientation relationship for α'/γ was very similar to that for γ/α' in the direct transformation and that the habit plane of the reversed austenite was close to $\{110\}_{\alpha'}$. Yakhontov⁽⁵⁵⁾ found that the twin disorientations in the martensite disappeared on reversion, and therefore concluded that the reversion process was the opposite of twinning. Sorokin⁽⁵⁴⁾ performed experiments with drawn Fe-Ni specimens, some of which contained retained austenite and some of which did not. He found that retained austenite accelerated the progress of reversion and also that specimens containing retained austenite produced a $\langle 111 \rangle_{\gamma}$ texture, and those not containing it produced a $\langle 211 \rangle_{\gamma}$ texture. He suggested that the reason for this behaviour was that retained austenite favoured that variation of the transformation which produced austenite oriented as closely as possible to the retained austenite. Shapiro and Krauss⁽⁵²⁾

suggested that the transformation was initiated by a {127} b.c.c. twinning deformation, the complex shuffles and twinning shears then setting in motion atomic movements which produced δ rather than twinned α' .

e) The effect of heating rate and Isothermal holding.

In stainless steels the only work on varying the heating rate seems to be by Smith⁽¹⁾ using a dilatometer. He suggests that a very slow heating rate (4.5°C/min) permits reversion to begin by a diffusional mechanism below the A_S temperature, with a shear mechanism then taking over at higher temperatures. He also suggests that very rapid heating may suppress stabilisation of austenite and so lower the A_S .

Jana and Wayman⁽⁴²⁾ found a similar effect in an Fe-34 Ni alloy, again using a dilatometer. With a heating rate of 1°C/min they found a gradual contraction between 200°C and 280°C, followed by an abrupt contraction at 280°C. At 4°C/min heating rate only the abrupt contraction at 280°C occurred. On temperature cycling, the gradual contraction was not found at 1°C/min on the second cycle. Also they found that holding isothermally between the A_S and A_f caused stabilisation of the α' , reversion not proceeding on further heating until a higher temperature was reached. They concluded that reversion occurred by a diffusionless process, possibly aided by a diffusion controlled process at slow heating rates. Kessler and Pitsch⁽⁴⁴⁾ confirmed that isothermal holding stopped reversion in an Fe-32.5 Ni alloy, but they decided that there were three effects

operating at slow heating rates. Firstly, there was an athermal process which was slow at first but then proceeded by bursting; secondly, at 400°C, when about 60% of the α' had reverted, this process stopped; thirdly, at 475°C, transformation continued and was complete at 550°C, but the product of this stage of the transformation was characteristic of a diffusion controlled process. They concluded that diffusion of Fe and/or Ni across the interfaces had resulted in the alloy composition around the interfaces approaching that of a two-phase region. Therefore the A_s was raised and reversion ceased.

Colling⁽⁷⁹⁾, working with an Fe-Ni-Co alloy, agreed with the graphs produced by Kessler and Pitsch, but he explained the gradual contraction at high temperatures in a different way. He stated that, as the temperature approached the Curie temperature of the γ , with reversion proceeding, a two-stage process occurred. Firstly the α' transformed to magnetic γ which had a low coefficient of expansion due to magnetostriction. Then, when the Curie temperature was passed a large expansion occurred due to the loss of magnetostriction. This expansion was large enough to counteract the contraction due to reversion, and so reversion appeared to stop. At faster heating rates only the abrupt contraction of α' transforming to non-magnetic γ was found. He pointed out that for the alloy used by Jana and Wayman T_c is about 210°C and that they found their gradual contraction between 200 and 280°C.

Zakharov et al⁽⁵⁶⁾ held specimens of Fe-30% and 32% Ni with various starting structures, at 400°C for up to

800 hours. The equilibrium structure of these alloys at 400°C had been calculated to contain about 27% α . In alloys which were initially austenitic very little α was found even after 800 hours. However, in specimens which had been previously quenched to form 84% α' , they found that cold rolling at room temperature caused reversion of 30% of the α' , and then 6 hours at 400°C left 27% b.c.c. phase in the specimen. They suggested that, in the austenite alloys, very fine layers of α formed martensitically but that the elastic stresses at the boundaries exceeded the elastic limit of the δ and caused plastic deformation which destroyed the coherency and stopped the transformation. In the quenched specimens, however, a large amount of martensite was able to form due to the higher values of the elastic limit at low temperatures. On reheating, some of the martensite reverted to austenite, leaving the equilibrium amount of b.c.c. phase at the reversion temperature.

Krauss and Cohen⁽⁴⁶⁾ found no stabilisation of austenite in iron-nickel alloys on up-quenching from room temperature to revert martensite. Later⁽⁶²⁾ they repeated this work using slower heating rates in a dilatometer. This time they found austenite stabilisation. with both the M_s and the amount of martensite produced decreasing on successive cycles. They also found that some of the b.c.c. phase was stable and not easy to revert. They concluded that a low-nickel ferrite had formed as a result of nickel build-up in the co-existing austenite; thus the M_s was lowered. Therefore, they decided that the stabilisation of austenite was due to nickel diffusion and not imperfections.

Golovchiner and Tyapkin⁽³⁵⁾ also found that very rapid heating, in a lead bath, caused less stabilisation than heating in air. However, they rejected the idea of diffusion since the specimens spent only a few seconds in the temperature range of the two-phase region. They concluded that stabilisation was caused by the fragmentation of the crystallites and that the elimination of this effect occurred faster on rapid heating in a similar way to that in which the temperature of recrystallisation is lowered, and recrystallisation speed increased by rapid heating.

Zel'dovich and Sadovskiy⁽⁸⁰⁾ used measurements of the Curie temperature to determine the nickel content of the austenite in an Fe-27Ni-2Ti alloy on isothermal holding. They found a redistribution of nickel between the martensite and the austenite even after only one minute; therefore, they concluded that the transformation was not purely martensitic. The lower the temperature, the faster was the rate of nickel redistribution, this redistribution occurring at temperatures below the A_s as well as above it. These workers also found that nickel redistribution occurred during continuous heating at $5^{\circ}\text{C}/\text{minute}$, resulting in austenite stabilisation, the M_s being lowered and less martensite forming at any given temperature. However, with rapid heating they found no nickel enrichment of the austenite although it was still slightly stabilised. This stabilisation was found to be related to the purity of the alloy and was attributed to the simultaneous existence of interstitial atoms and lattice defects introduced by the transformation.

Berdova et al⁽⁸⁷⁾ also found stabilisation of austenite on holding quenched Fe-Ni-Mn-Cr-C alloys below the A_s . They suggest that, in the first stages of martensite formation (the M_s was about 200°C), the γ/α' interface was coherent and the γ at the interface was therefore elastically extended. Then, on re-heating, carbon diffused into γ , thus lowering the M_s . In an alloy in which more α' formed on soaking isothermally, the γ was constricted by a network of α' plates and stabilisation was then controlled by mechanical hardening and elastic stress relaxation.

Nagpaul and West⁽⁷⁵⁾ found that prolonged austenitising of an Fe-Ni-C alloy produced a magnetic response, and they attributed it to the formation of a $\gamma + \alpha +$ carbide structure.

Ankara⁽⁷⁸⁾, working with an Fe-30Ni alloy, varied the heating rate and reversion temperature. At slow heating rates he found the highest strength resulted from the lowest reversion temperature, but at rapid heating rates, the highest strength was found at a temperature over 100°C above the lowest reversion temperature. He suggested that three factors are involved, namely: the dislocation density, the cell size, and the cell misorientation. At rapid heating rates a higher temperature is needed to increase the mobility of the dislocations, which allows the cell boundaries to move and unite, thus increasing their misorientation. This results in the strength increasing with temperature until a critical value is reached where the decrease in dislocation density due to recovery, and the

increase in cell misorientation above a critical value, cause softening with increasing temperature. The M_s was found to depend only on the dislocation density.

f) The effect of Plastic Deformation on Reversion

Smith⁽¹⁾ found no difference in the progress of the reverse transformation in stainless steels whether the α' had been formed by quenching to -196°C or by deformation. In particular he found that the A_s and A_f were unaffected by the mode of formation of the α' .

In Fe-Ni-V and Fe-Ni-Ti alloys, Golovchiner⁽³⁴⁾ found that the mechanism of the reverse transformation depended on the state of the α'/δ interface. If the accommodation state of the interface had been disturbed by cold work or precipitation, then the reverse transformation did not retrace the path of the direct transformation, different surface tilting effects being observed.

Mel'nikov et al⁽⁴⁹⁾ found that deformation of an Fe-Ni alloy at room temperature retarded reversion, but that deformation just below or above the A_s enhanced reversion. However, when reversion had been initiated by deformation below the A_s , it was found that, on raising the temperature, further reversion did not occur until the temperature was well above the A_s . Thus deformation affected the reverse transformation in the same way as it does the direct transformation in such alloys, i.e. transformation can be stimulated or retarded depending on the temperature of deformation. Mel'nikov et al therefore concluded that the reason for both effects was the same.

Sokolov et al⁽⁵³⁾ investigated various Fe-Ni alloys. They found that prior deformation lowered the A_s in 9% and 12% Ni alloys, had no effect in an 18% Ni alloy, and raised the A_s in a 27.6% Ni Alloy. They concluded that, with the slow heating rates which they used, the transformation was diffusion controlled in the low nickel alloys.

Zaytsev and Gorbach⁽⁵⁷⁾ found that reversed austenite formed from deformed α' inherited the extra defects from the deformation and was thus strengthened. However, the rate of softening of this stronger reversed austenite was much faster than that of reversed austenite formed from quench-induced α' .

Harvey⁽⁸¹⁾, however, found that reversed austenite formed from deformed α' was very little stronger than that from undeformed α' , and concluded that the transformation could sweep away any defects present before it occurred.

Zel'dovich and Sadovskiy⁽⁸⁰⁾ found that the influence of deformation on the reverse transformation appeared to relate to structural changes in the alloy, in that it disturbed the coherency of the α' and retained γ , it increased the dispersion of phase components, and it increased the dislocation density.

1.4. Transformation Cycling.

Transformation cycling has been used by a number of workers^(76,82) to refine the austenite grain size. There is a large effect of initial microstructure on this grain refinement, martensite producing much finer grained γ on reversion than ferrite + pearlite structures. The reason for this seems partly to be that lower austenitising temperatures are needed for martensite, and partly that martensite provides many more nucleation sites for γ than does a ferrite + pearlite structure, particularly at the α' grain boundaries. Grain refinement can be enhanced by the presence of a fine precipitate dispersion which inhibits grain growth. The finest grain size obtainable seems to be about $1\mu\text{m}$.

The phenomenon of stabilisation of γ after reversion was mentioned earlier; this has been found to occur progressively with successive transformation cycles from α' to γ . In stainless steels Smith⁽¹⁾ found, in a 16/12 alloy, that γ stabilisation increased with successive cycles, although the magnitude of the effect decreased with each cycle. Breedis⁽⁵⁹⁾ working with a similar steel, found that heating for two minutes just below the A_s increased the α' content on requeenching, by 50%. However, heating above the A_s caused stabilisation of the γ , this being less after 2 hours than after 2 minutes. He attributed the increase in α' to the relief of internal strains, observing that dislocations, stacking faults and twins between the α' crystals comprising a lath, disappeared after 2 minutes at 500°C . The γ stabilisation at higher temperatures he

attributed to the defect structure in the reversed austenite hindering the development of an α' lath. In some earlier work, Breedis and Robertson⁽¹⁷⁾ found no γ stabilisation in a 16/12 stainless steel, and also found that the second generation α' formed in the same sites as the first. However, in this case, reversion had been performed for 15 minutes at 900°C which allowed time for almost full recrystallisation of the γ .

They concluded that the nucleation of the martensite was heterogeneous.

Malyshev et al⁽⁴⁸⁾ found almost complete austenite stabilisation after two cycles of transformation in an Fe-10Cr-14Ni alloy. However, they found virtually no stabilisation in an Fe-28Ni alloy. In both alloys, however, the first cycle produced a large increase in yield stress, but following cycles only produced small increases. They concluded that the effect on the yield stress was caused by the refinement of the block size of the austenite, which changed very little after the first cycle. The stabilisation, they decided was caused by elastic distortions of the lattice which were stable in the Fe-Cr-Ni alloy, but were removed in the Fe-Ni alloy by recovery at reversion temperatures.

Golovchiner and Tyapkin⁽³⁵⁾ found that reversion lowered the M_s in an Fe-Ni alloy, but raised it in an Fe-Ni-Ti alloy. However, in both alloys the martensite content after the second quench was less than after the first; also the transformation was more sluggish the second time. Raising the austenitising temperature decreased these effects. Deformation had a similar effect to that of reversion in

the Fe-Ni alloy, but also caused austenite stabilisation in the Fe-Ni-Ti alloy. Although stabilisation was eliminated by increasing temperature, this elimination did not coincide with recrystallisation. They, therefore, concluded that the stabilisation was associated with the fragmentation of crystallites.

Smith⁽¹⁾ found that the hardness of a 16Cr/12Ni steel increased with transformation cycling, the hardness being doubled after four cycles. There was a tendency for the effect to level off after two cycles, which he attributed to the progressively smaller volume fraction of additional reversed austenite produced in successive cycles. The hardness increase, he decided, was due to an increase in the density of the defect structure of the reversed austenite due to inheritance of defects from successive generations of martensite, and the production of defects by the reverse transformation.

Edmondson and Ko⁽³³⁾ found complete stabilisation after fifteen cycles of treatment in an Fe-34 Ni alloy. They also found successive generations of martensite to form in different sites from previous generations. They, therefore, concluded that deformation, resulting from reversion, rendered the martensite nuclei ineffective. Caron and Krauss⁽⁸³⁾ however, found that successive generations of martensite in an Fe-30 Ni alloy, formed in the same sites, although the second generation martensite plates were smaller and narrower than the first generation. They found that cycling caused the M_s to rise, but the amount of martensite formed at -196°C to fall progressively with each cycle. They concluded that

cycling introduced preferred nucleation sites for martensite, but that the dislocation tangles and closely spaced boundaries restricted the motion of the interface, and thus inhibited the growth of the nuclei and reduced bursting.

Bolton et al⁽⁶³⁾, from work on Fe-Mn alloys, suggest that, in low S.F.E. materials, after deformation or reversion, dislocation pile-ups are present which produce elastic stresses which counteract stresses induced by transformation; thus the martensite transformation is enhanced. In high S.F.E. materials, however, a cell network forms, the boundaries of which act as a barrier to the progress of the transformation. They support this by the fact that when Fe-Mn alloys, which have a low S.F.E., are reverted dislocation pile-ups are formed which stimulate the transformation to martensite. However, if the austenitising time or temperature is increased, thermally-activated cross-slip occurs, producing cell networks which cause the M_s to fall.

Similar ideas were expressed by Jordan and Borland⁽⁴³⁾. They found the M_s of an Fe-Ni alloy to decrease with increasing reversion temperature, and suggested that residual stresses in reversed austenite cause the elastic strain energy associated with martensite formation to be relieved by plastic flow. Thus, whether reversion enhances or retards subsequent α' formation depends, in part, on the relative magnitudes of the flow stress of the alloy and the transformation stresses. Once the recrystallisation temperature was reached they found that the M_s began to rise again.

Different results were obtained by Sastri and West⁽⁸⁴⁾ investigating the kinetics of α' formation from various δ grain sizes and dislocation densities, in certain medium alloy steels and Fe-Ni alloys. They found that the M_s decreased with increasing δ yield strength, and concluded that the main factor affecting the kinetics of α' formation was not the prior δ grain size, but the defect structure of the δ . They considered that the number and size of martensite embryos, and their subsequent propagation, depended on the dislocation density of the δ . A high δ dislocation density was associated with a low M_s and a high initial rate of α' formation. The reason suggested for this was that, at high dislocation densities, a larger number of α' embryos were present, but their propagation was inhibited by an increase in the strain energy associated with transformation. Ankara and West⁽⁸⁵⁾, working with the same alloys, found transformation plasticity to be inversely proportional to the δ yield strength, and used the equation derived by Johnson and Greenwood⁽⁸⁶⁾ to explain this in terms of macroplasticity. They suggested that the influence of reversed austenite on subsequent transformation to α' is due to the increase in the δ yield strength.

In alloys containing carbon an added complication is posed by the precipitation of carbides. Hyatt and Krauss⁽³⁹⁾ found that two processes occurred during transformation cycling of a medium carbon steel. Firstly, there were normal reversion processes, and, secondly, recrystallisation produced a small δ grain size. Using Fe-Ni-C alloys they found that alloys with less than 0.3% C behaved in a similar manner to

binary Fe-Ni alloys, but alloys with more than 0.3%C yielded large variations in strength after cycling due to carbide precipitation removing carbon from solution. Habrovec et al⁽³⁸⁾ plotted the strength of second generation α' formed by quenching to -196°C against reversion temperature for an Fe-Ni-C alloy, and found two peaks. At the first, and highest peak they found needle-like low-carbon martensite since precipitation in the austenite had depleted the matrix of carbon. At the second peak less carbon had been precipitated and the martensite was coarse and plate-like. Malyshev et al⁽⁴⁸⁾ found that, when using an Fe-Mn-Cr-Ni alloy containing 0.6%C where the A_f was near to the recrystallisation temperature, recrystallisation developed with cycling.

Using a maraging steel, Goldberg⁽⁶⁴⁾ found that no change in the M_s , A_s or A_f occurred on transformation cycling with high heating rates. At slow heating rates, however, precipitation occurred and the A_s decreased, and the A_f and M_s increased with cycling. He concluded that segregation had occurred and that reversed austenite nucleated at precipitates, the A_f and M_s increasing due to solute depletion in the matrix.

Also using a maraging steel, Saul et al⁽⁸⁸⁾ found that thermal cycling produced a refined austenite grain size. They suggested that this refinement was due to the shear strain produced by reversion causing increased nucleation of recrystallised austenite grains. They believed that the finer α' grains, produced from the finer grained γ , were the reason for the continued refinement of the γ grain size on

successive cycles, until a limiting size was reached at which the strain energy available for nucleation of recrystallised grains was not sufficient to cause further refinement.

15. Precipitation during reversion.

Aspects of precipitation related to thermal cycling have been dealt with in the previous section.

Carbide precipitation in austenite raises the M_S of steels, and studies in stainless steels have shown that the M_S can be raised sufficiently for some retransformation to α' to occur on returning to room temperature after reversion. Thomas and Krauss⁽⁵⁸⁾, after reversion of an 18/8 stainless steel, found precipitates of $M_{23}C_6$ throughout prior regions of α' . They believed that the precipitation occurred just prior to reversion and enhanced the formation of α' on cooling. They supported the claim that the precipitation occurred in α' by comparing the morphology of the $M_{23}C_6$ to that of Fe_4N precipitates in b.c.c. iron. Smith⁽¹⁾ found precipitation of $M_{23}C_6$ in a 15/9 stainless steel to occur first at grain and twin boundaries, and then later in the laths of reversed austenite. In cold worked and reversed structures he found extensive precipitation to occur very rapidly resulting in the raising of the M_S above room temperature. He suggested that depletion of carbon and chromium from the matrix changed its composition to correspond to a two-phase structure of $\alpha + \gamma$, and consequently some ferrite formed by a diffusional process at high temperatures. Smith attributed the strength increase after precipitation to the increased α' content, although Malyshev⁽⁴⁸⁾ attributed some of the increase in an Fe-Mn-Ni-Cr alloy to the precipitates themselves.

In an Fe-Ni-C alloy, Gorbach et al⁽³⁶⁾ found that, at rapid heating rates, reversion occurred by a diffusionless

transformation and strengthening resulted. At slower heating rates, however, precipitation depleted the matrix of carbon and no strengthening resulted. They decided that the critical heating rate necessary for strengthening depended on the temper-resistance of the α' and the temperature range of reversion.

Nagpaul and West⁽⁷⁵⁾ found no evidence of precipitation after short time reversion treatments in Fe-Ni-C and Fe-Ni-Mo-C alloys, in which reversion was complete within one second. However, they identified cementite by electron diffraction after tempering the α' for 15 seconds at 550°C. Also they found that prolonged austenitising produced a ferromagnetic response which they suggest was due to the formation of a $\gamma + \alpha + \text{carbide}$ structure.

There have been two papers on precipitation in Fe-Ni-Ti alloys, Golovchiner⁽³⁴⁾ found that the strength of a quenched specimen just after reversion was greater than that of a cold worked specimen containing martensite. However, this was not found to be so with an Fe-Ni-V alloy. The idea of the precipitation of a Ti-rich disperse phase, in either γ or α' , was dismissed due to the very short times that the specimens were in the precipitation temperature range. He concluded that the effect was due to the third element disturbing the accommodation state of the α'/γ interface, thus changing the mechanism of the transformation. In support of this, he found that, in Fe-Ni alloys with V, Co or Cu added, the surface relief after reversion was a mirror image of that produced by the formation of α' ; whereas, in alloys with Ti or Al added, the

relief after reversion was more complicated than that after the formation of the α' . Gorbach et al⁽³⁶⁾, however, investigated reversion in Fe-Ni-Ti alloys using X-Rays and found that the fine structure after reversion was slightly coarser in alloys containing Ti than in those without it. They therefore attributed the high strength after slow heating to reversion coupled with precipitation. They also decided that the greatest contribution to ageing was made in the austenitic state.

Harvey⁽⁸¹⁾, working on certain ausforming steels, found that γ formed from aged, strain-induced α' , could be made to inherit a fine dispersion of second phase particles from the α' . This provided extra strengthening, and also the particles somewhat delayed recrystallisation^a. Reversion of the α' sometimes caused loss of coherency of the carbide particles. The presence of the fine particles during the shear transformation caused multiplication and tangling of lattice defects by interaction with the particles, and a fine grained structure was formed due to the large number of nucleation sites. The dispersed particles caused locking of the dislocations and rendered them immobile, whereas, without the presence of the particles many of the dislocations in unaged, cold worked α' were 'swept out' by the progress of the reverse transformation, since they were mobile.

CHAPTER 2.

EXPERIMENTAL PROCEDURE.

2.1 Alloy Preparation.

All of the alloys were vacuum melted by the International Nickel Company Ltd. Alloys A₁ and B were received as $\frac{3}{8}$ " thick, hot-forged plate. Alloys A₂ and C were received in ingot form and were subsequently hot forged to 2" thickness followed by hot rolling to $\frac{3}{8}$ " thickness. Their compositions, in weight per cent, were as follows:

Alloy A₁:

Fe	C	Cr	Ni	Mo	Al	Si	Mn	S
bal	0.002-0.003	16.1	11.7	0.01	0.01	0.02	0.05	0.007
P	Cu	Ti	Co	V	Pb	B	Zr	Mg
0.003	0.05	0.05	0.10	0.02	0.001	0.002	0.01	0.01

Alloy A₂:

Fe	C	Cr	Ni	Mo	Al	Si	Mn	S
bal	0.003	16.2	12.0	0.01	0.01	0.1	0.1	0.005
P	Cu	Ti	Co	V	Pb	B	Zr	Mg
.002	0.1	0.05	0.1	0.02	0.001	0.002	0.01	0.01

Alloy B:

Fe	C	Cr	Ni	Mo	Al	Si	Mn	S	P
bal	0.09	14.9	8.7	2.05	0.01	0.05	0.05	0.002	0.002

Alloy C:

Fe	C	Cr	Ni	Si	Mn	S	P	Cu
bal	0.005	16.5	10.2	0.1	0.1	0.004	0.004	1.8

2.2 Fabrication and Heat Treatments.a) Homogenising.

Strips approximately 4" x 1" x $\frac{3}{8}$ " were cut from the plates and 0.05" of each surface was removed by milling. The strips were then rolled at room temperature to a thickness of 0.2". Homogenising was then performed under a dynamic vacuum for 24 hours at 1100°C for all alloys, followed by furnace cooling under vacuum.

b) Rolling and Intermediate heat treatments

0.01" was then chemically removed from each surface by immersing the strips in a warm solution containing 50% HCl, 10% HNO₃, 5% H₃PO₄, 35% H₂O. All alloys were then rolled to produce a 50% reduction in thickness at room temperature. At this stage the specimens were approximately 0.1" thick and for all further heat treatments in air furnaces they were sealed in silica tubes under a partial atmosphere of argon.

A standard pattern of 50% deformation by rolling followed by solution treatment was then adopted for all alloys until the required thickness was obtained. The solution treatments were performed in a vertical crucilite rod furnace by suspending the specimens by Kanthal wire

attached to two fuse wires at the water-cooled top of the furnace. Rapid quenching was attained by cutting the fuse wires, thus allowing the specimens to fall through the aluminium foil seal at the bottom of the furnace into a bucket of water placed beneath it. The silica capsule was smashed directly on entering the water thus allowing a rapid quench. After each heat treatment 0.01" was removed from each surface of the specimen chemically, as previously described.

The solution treatments performed for alloys A and C were 20 minutes at 1050°C, and a period of 10 minutes was allowed for the specimens to reach the treatment temperature.

The solution treatment for Alloy B was one hour at 1250°C, again with 10 minutes allowed for the specimens to reach the temperature. The higher temperature for this alloy was necessitated by the higher carbon content. In general the solution treatment times and temperatures were determined by consideration of the grain size produced and its consequent effect on subsequent transformation to martensite and mechanical properties. An average austenite grain diameter was obtained of about 40 μm in each case.

c) Quench-Induced Martensite.

Partial transformation to martensite was obtained in alloys A and C by quenching specimens, after solution treatment, to -196°C for 15 minutes. Liquid nitrogen was used to obtain -196°C. Treatments at higher sub-zero temperatures were carried out by immersion in various

mixtures of acetone and liquid nitrogen. These mixtures could be kept to $\pm 3^{\circ}\text{C}$ for periods of 15 minutes.

d) Deformation-Induced Martensite.

Various amounts of martensite were produced in each alloy by the 50% rolling treatments at room temperature. Larger amounts of martensite were produced by the standard 50% deformations at temperatures below room temperature. Various mixtures of acetone with liquid nitrogen or solid CO_2 were used to produce the sub-zero temperatures, and an ice-water mixture was used for treatments at 0°C . The specimens were immersed in the solutions initially and allowed 5 minutes to attain the required temperature; they were then rolled 0.01" or less at each pass through the rolling mill, and replaced in the solutions in between passes to allow them to re-cool to the temperature required.

Some specimens of alloy B were rolled at $+100^{\circ}\text{C}$ and $+150^{\circ}\text{C}$, boiling water and an oil bath respectively being used to attain these two temperatures.

e) Reversion, Annealing and Ageing treatments.

Reversion treatments were generally carried out by plunging the specimens into a salt bath at the required temperature, suspended on a wire. Small disc specimens for electron microscopy were contained in a gauze cage for these treatments. All specimens were water quenched after reversion treatments.

Isothermal treatments of alloy A and ageing treatments of alloy C were also generally carried out in salt baths,

although some of them were carried out in horizontal tube furnaces with the specimens sealed in silica under a partial atmosphere of argon. Specimens were also water quenched after treatments in the air furnaces, the silica tubes being smashed in the water to facilitate a rapid quench.

The salts used in the salt baths were an equal mixture of KNO_3 and NaNO_2 for treatments at 600°C and below; and "Cassel 660" for treatments at 650°C or above.

f) Magnetic Measurements.

Room temperature measurements of specific magnetic intensity, and hence of martensite content, were made using a Sucksmith ring balance, details of which are given in Appendix A.

Specimens approximately $\frac{1}{4}$ " x $\frac{1}{4}$ " x 0.025" were cut from cold rolled strip using a guillotine, and their centres were drilled using a No. 50 drill. The specimens were then given the heat treatments appropriate to the experiment in hand, after which the surface layers were removed chemically to a depth of about 0.01".

The specimens were weighed and their displacements measured under the influence of a field gradient produced by an electromagnet in the ring balance. By comparison with the displacement of a pure-iron specimen of similar weight, it was possible to evaluate the specific magnetic intensity of the specimens and hence their martensite content. The small contributions to the measured specimen deflections arising from the weakly paramagnetic nature of

the specimen holder and the influence of the magnetic field on the transducer meter were eliminated from the recorded results by taking a 'zero' reading under the normal operating conditions, using a specimen holder but no specimen.

Specimen to specimen variations were often apparent which exceeded the reproducibility of readings on a given specimen. These variations were attributed to the inherently inhomogeneous nature of the martensite transformation, and, therefore, their effect was minimised by taking readings on three or more specimens for each condition. An average value was then calculated.

It is known⁽¹⁰⁴⁾ that a strong magnetic field can enhance the transformation of austenite to martensite in steels. There existed, therefore, the possibility of specimens undergoing martensitic transformation during magnetic measurements. The magnitude of this effect is fairly small, and since the M_s temperatures of all the alloys were about 70°C below room temperature it is felt that room temperature measurements were unlikely to produce any transformation to martensite.

It is suggested in the work on the isothermal transformation of martensite to austenite that the magnetic phase underwent a compositional change in a certain range of temperature and time. If this was the case, then the change in composition would have caused a change in the value of the specific magnetic intensity of the magnetic phase, which, in turn, would have resulted in an inaccuracy in the calculated amount of the magnetic phase. In the

present work it is felt that the shape of the graphs determined magnetically (Fig. 3.1) was confirmed by the hardness and dilatometry results (Figs. 3.2 and 3.3), and therefore that the general conclusions drawn are not invalidated by the inaccuracies which may have been present in the specific values of magnetic phase content.

g) Hardness Measurements and Light Microscopy.

Specimens approximately $\frac{1}{2}$ " x $\frac{1}{2}$ " x 0.05" after heat treatment were used for both hardness measurements and light microscopy. 0.01" was removed chemically from each surface and then one surface was polished on silicon carbide papers. Hardness measurements were then made using a Vickers diamond indenter with a 10 Kg load or 20 Kg on cold worked specimens. Average values were obtained from at least two specimens for each heat treatment, at least 5 indentations being made on each specimen.

Specimens for light microscopy were further polished using diamond paste on rotating wheels down to 1μ m particles. The specimens were etched in a solution of 3 parts HCl, 1 part HNO₃ and 2 parts glycerol for approximately 10 seconds. This solution began to fume if kept for longer than 2 hours, and so was freshly made for each experiment.

h) Mechanical Property Measurements.

Tensile tests were carried out on strip specimens of about 0.05 cm. thickness, using a 2 cm gauge length of width about 4.8 mm. An Instron machine was used at a cross-head speed of 0.1 cm/min; the usual machine corrections were made.

Compression tests were carried out on specimens approximately 6mm x 2mm x 2mm, again in an Instron machine at a cross-head speed of 0.005 cm/min.

In both types of test the specimens were machined from cold rolled material prior to heat treatment. Their surfaces were then polished on 600 grade-silicon carbide paper and their dimensions measured before testing.

Since these steels are known⁽¹⁰⁷⁾ to transform partially to martensite during testing at room temperature most of the tests were carried out at +150°C in a silicone-oil bath. Austenitic samples were found not to be magnetic after testing at this temperature.

Values of the 0.2% or 0.1% proof stress were calculated from both tensile and compression tests, and also values of the ultimate tensile stress and % elongation were calculated from the tensile tests.

1) Dilatometry.

Dilatometric measurements were made using a differential technique (see Appendix B) during isothermal holding, continuous heating, and continuous cooling. Specimens of alloy A were investigated, their expansion or contraction being continuously compared with that of a fully austenitic specimen of the same alloy in the investigations into the reverse martensite transformation; and with a partially martensitic alloy, which had been quenched 5 times for 1 hour at -196°C, in the case of investigations into the direct martensite transformation.

In the case of the isothermal transformations, the

furnace was first set at the required temperature, and then the specimens were placed in position and the furnace moved until the specimens were in the hot zone.

For the measurement of A_s and A_f temperatures the furnace was set well above the expected A_f , at about 750°C , and then placed about the specimens, the expansions and contractions were then observed during heating. Heating rates obtained by this method were about $80^{\circ}\text{C}/\text{minute}$.

For the measurement of M_s temperatures the specimen tube was immersed in a dewar flask containing isopropane, and liquid nitrogen was poured slowly into the isopropane, with continuous stirring, resulting in a gradual fall in temperature. The lowest temperature obtained by this method was -80°C , which was attained at a cooling rate of about $2^{\circ}\text{C}/\text{minute}$. A rapid contraction was observed when the transformation to martensite began, and the presence of martensite was confirmed magnetically.

j) Electron Microscopy.

Discs of 2.3 or 3 mm diameter were punched from cold-rolled sheet 0.02" thick. The discs were then heat treated as required, after which they were ground on silicon carbide paper using rotary wheels, to a thickness of 0.005", both sides of the discs being equally ground. In order to hold them for grinding the discs were attached to a perspex sheet using double-sided selotape.

A jet profiling technique was then used as the first of the two stages of the thinning process. The disc was held horizontally in a PTFE holder and a solution of 40%

HCl in water was directed onto the specimen. A potential of 60 volts produced a current of about 0.5 amps and was applied for 5 seconds on each side of the specimen. Final thinning in a saturated solution of chromium trioxide in orthophosphoric acid, cooled by an ice + water mixture, at 12 volts (about 0.4 amps) produced perforation at the centre of the disc after 1-2 minutes.

The specimens were washed by directing a jet of water tangentially onto their surface down a pair of tweezers followed by a similar washing in Methyl Alcohol, and then dried between sheets of absorbent tissue. The specimens were then stored in gelatine capsules and kept in a dessicator until required.

CHAPTER 3.

THE ISOTHERMAL TRANSFORMATION OF MARTENSITE TO AUSTENITE.

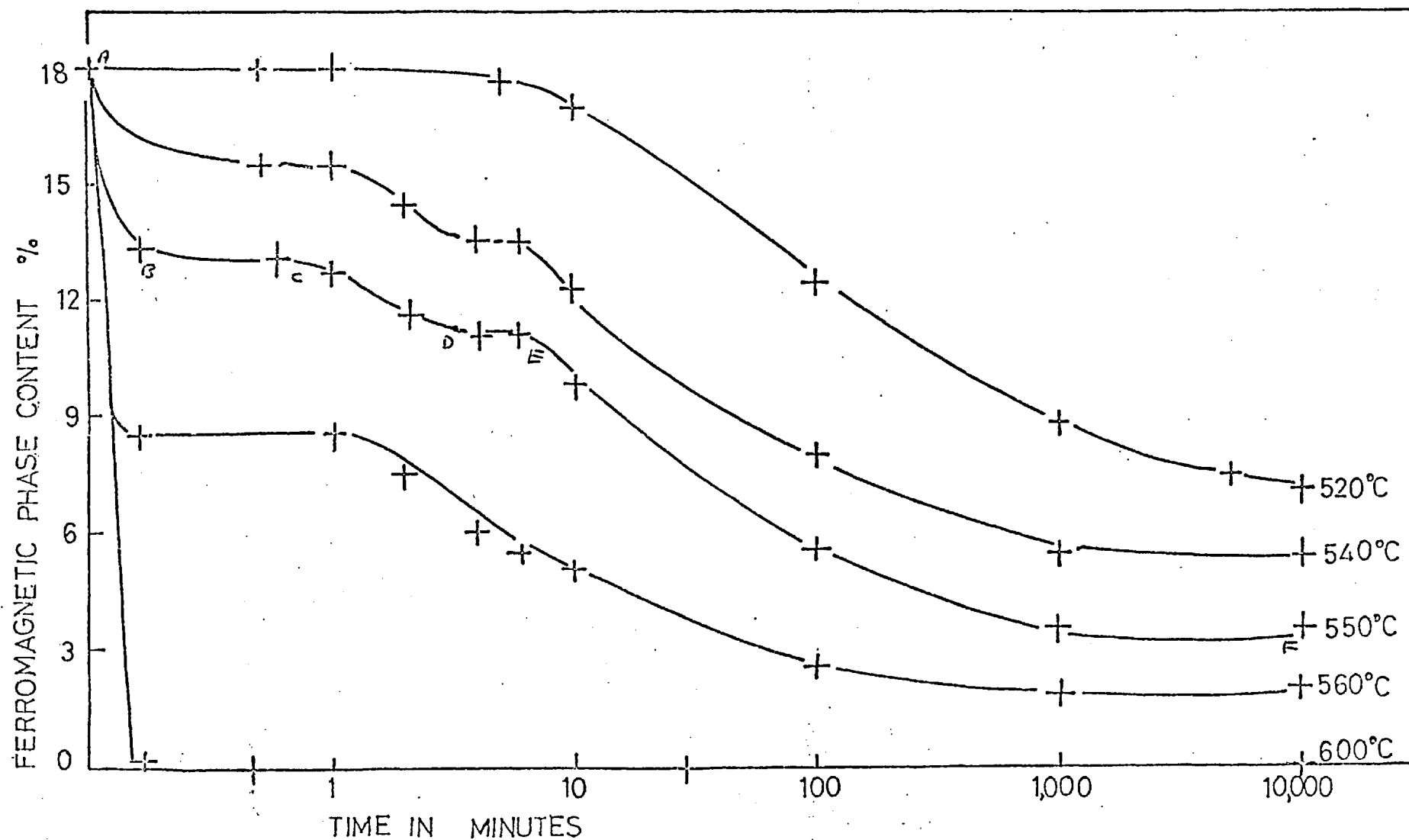
3.1 RESULTS

3.1.1 Kinetic Aspects

The transformation of martensite to austenite in alloy A, under conditions of isothermal holding, has been investigated at temperatures between A_S and A_f and below A_S . The transformation was followed using magnetic measurements, hardness measurements and dilatometry. The experiments were performed by plunging specimens into a salt bath, set at the appropriate temperature, which resulted in the initial heating rates being rapid. The specimens were quenched into water after heat treatment.

Fig. 3.1 shows the variation in ferromagnetic phase content on isothermally holding, quench-induced martensite at various temperatures, above and below A_S . The relationship between ferromagnetic phase content and isothermal holding time was found to be very temperature dependent, a temperature increase of 3 or 4°C causing a decrease of 2 or 3% martensite in the early stages of transformation at temperatures of 550°C and above. This caused a scatter in the points on the graph of up to $\pm 1\%$ martensite. However, the experiment was carried out five times between 540°C and 550°C and the shape of the graph was the same in each case, although the actual values differed.

It appeared that, at 550 C,^o the ferromagnetic phase



3.1. Alloy A. Changes in ferromagnetic phase content on isothermal treatment of quenched, partially martensitic structures.

content decreased in three stages, whilst at 520°C only the third stage occurred, and at 560°C only the first and third stages occurred. The stages are marked on the graph for 550°C as AB, CD, EF. The first stage, which comprised the whole transformation at 600°C , i.e. just above the A_f , occurred very rapidly and was complete, for specimens 0.02" thick, within 20 seconds. The time taken for completion of this stage was found to depend on the thickness of the specimens. The thicker the specimen the longer the first stage took to reach completion. This effect was attributed to the time taken to reach the temperature of the salt bath. Surface tilting was observed in polished specimens heated to 600°C in a high temperature optical microscope, indicating that a shear transformation was involved. The amount of transformation occurring in the first stage increased with increasing temperature.

Following the first part of the transformation there appeared to be an "incubation period" of approximately one minute before a second reaction began, which involved a further decrease in the ferromagnetic phase content. This second reaction exhibited isothermal characteristics, only appeared between 530°C and 550°C , and was complete after approximately ten minutes. At 520°C and below, the second reaction was either non-existent or too small to be detected, and at 560°C and above, it was overlapped by the early development of a third reaction.

The third reaction, illustrated by points E to F in Fig. 3.1, was found to occur at all the temperatures below 600°C shown in Fig. 3.1, and also at lower temperatures down

to 430°C. It seemed to require an incubation period of several minutes, this being shorter at higher temperatures, and then reached completion after 100 minutes at 560°C, but required two weeks for completion at 430°C. After completion of this third reaction no further change in ferromagnetic phase content was found to occur on holding for up to three months at the transformation temperatures.

Fig. 3.2 shows the hardness changes associated with the transformation at 550°C. Although a large scatter was found in the hardness results ($\pm 5H_v$) the general shape of the graph was determined quite reliably. It can be seen that the hardness decreased in the same fashion as the magnetic phase content decreased. The first reaction took longer to complete as determined by hardness measurements. Presumably this was due to the larger size of the specimens used for hardness as compared with magnetic measurements.

Comparing Fig 3.1 and Fig. 3.2, the hardness decrease per percentage decrease in magnetic phase can be seen to have been different for each of the three stages. In stage one the hardness fell approximately 4 Hv per percent decrease in magnetic phase, and in stages two and three the decreases were 3.5 Hv and 2 Hv respectively. This result was somewhat unexpected since there was time for much more recovery to take place in stage three than in stage one.

Fig. 3.3 shows dilatometer curves for isothermal holding at 550° and 560°C. The part of the dilatometer experiments before the specimens reached the test temperature had to be ignored, due to anomalous effects caused by the different surfaces of the test and control specimens. This

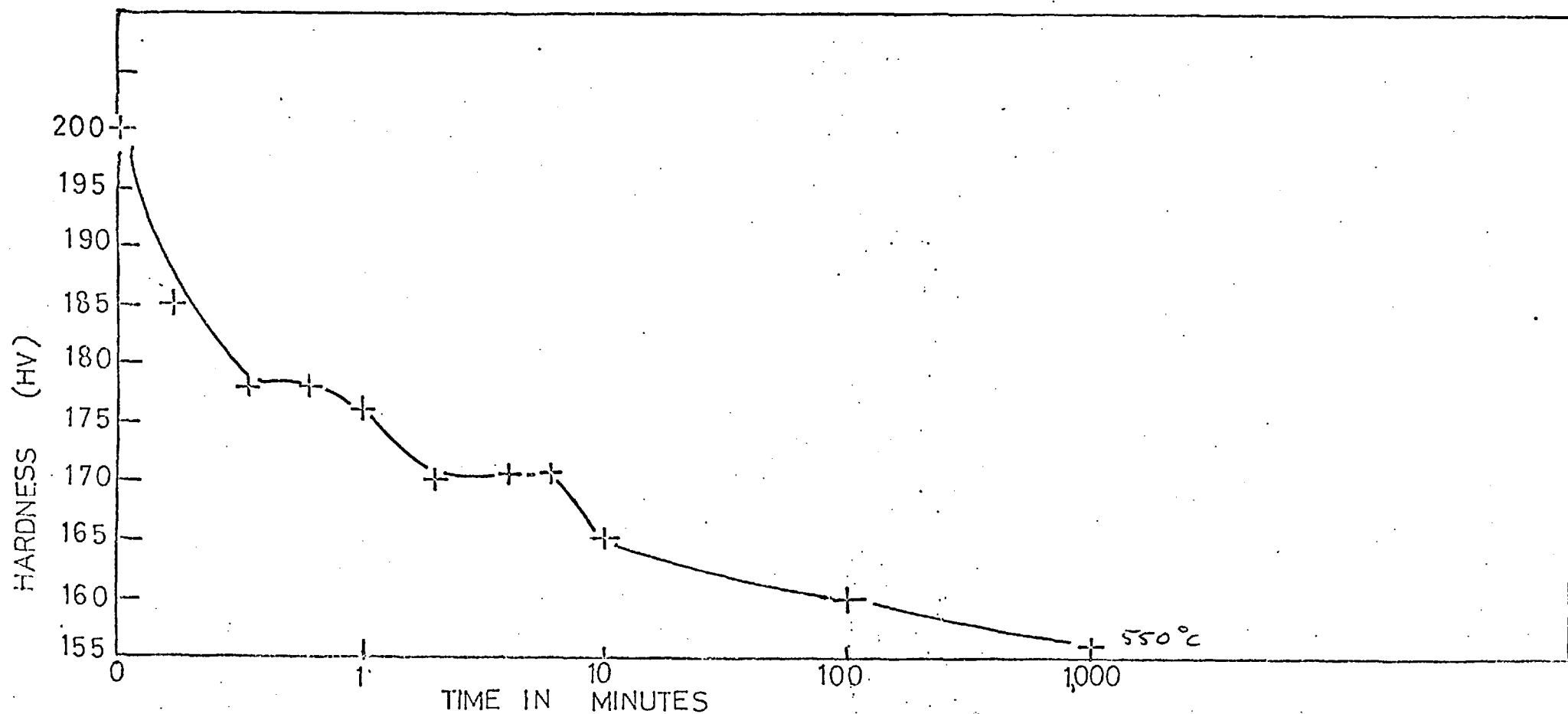


Fig. 3.2 Alloy A. Changes in hardness on isothermal treatment of quenched structures.

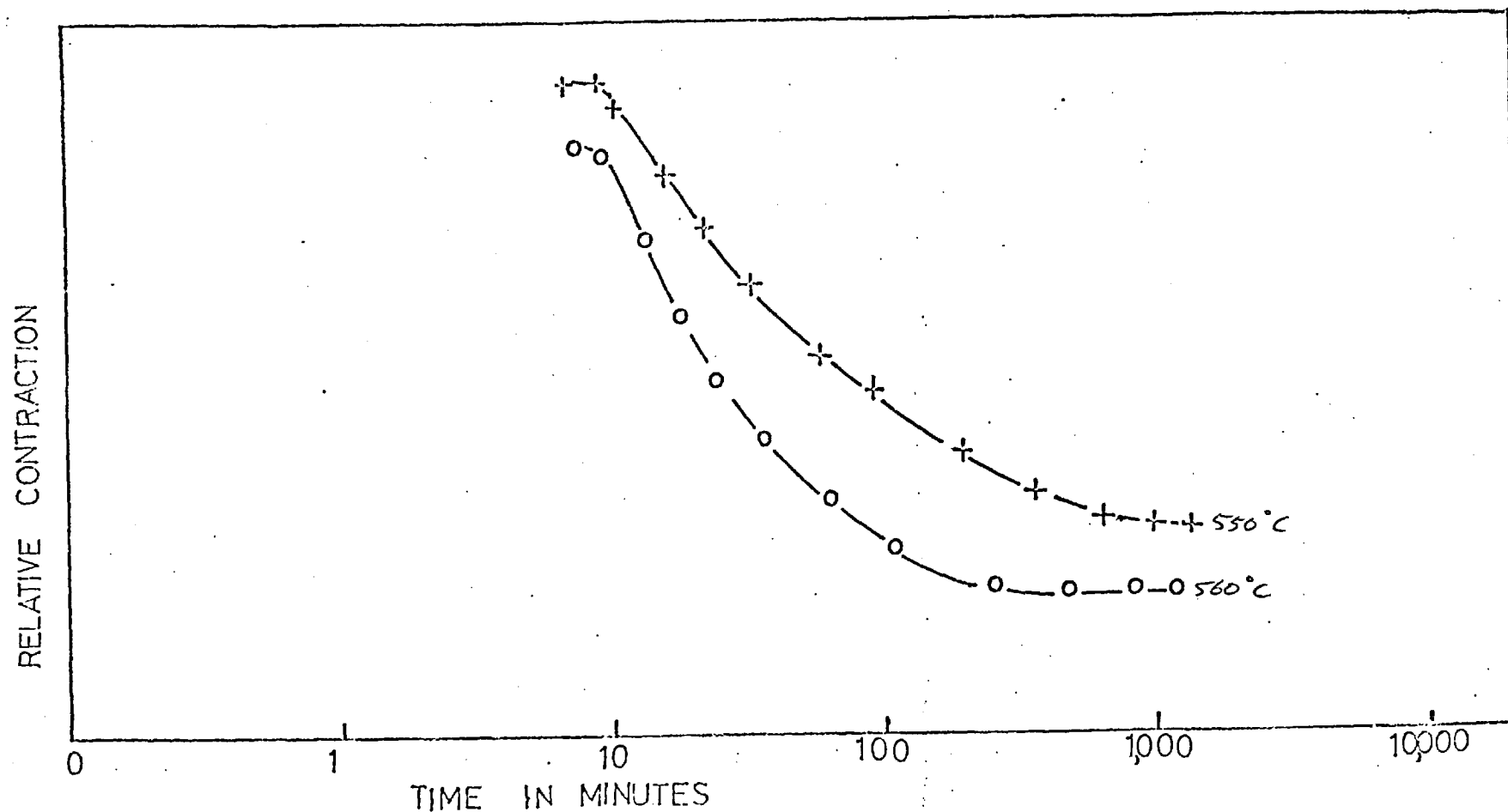


Fig. 3.3 Alloy A. Relative contraction of partially martensitic structures compared with fully austenitic structures on isothermal treatment at 550 and 560°C.

meant that, since the fastest heating rate obtained in the dilatometer was 60°C per minute, stages one and two of the magnetic curves could not be detected, since stage three had begun by the time the test temperature was attained. However, the occurrence of stage three was confirmed by an overall contraction shown in Fig. 3.3; these curves agree very well with Fig. 3.1 with regard to the times of transformation of stage three.

Figs. 3.4 and 3.5 show the effects of similar isothermal heat treatments to those described above, on deformation-induced martensite. Fig. 3.4 was produced from specimens of alloy A deformed 50% at room temperature, thus producing approximately 10% martensite; and Fig. 3.5 was produced from specimens deformed 50% at -78°C , thus producing approximately 70% martensite. The general shape of the graphs for the deformation-induced martensite was similar to that for quench-induced martensite. There were, however, certain differences which were noted. Firstly, in Fig. 3.4, for room temperature deformation-induced martensite, the final percentage of stable magnetic phase was less, at both temperatures, than it was for quench-induced martensite; in fact, at 550°C no stable magnetic phase remained after 10,000 minutes. However, in Fig. 3.5, for martensite induced by deformation at -78°C , the final percentage of magnetic phase was higher at 520°C than it was for quench-induced martensite at that temperature. Thus, although the amount of magnetic phase may have been affected by the mode of formation and the amount of deformation of the martensite, it seems that the

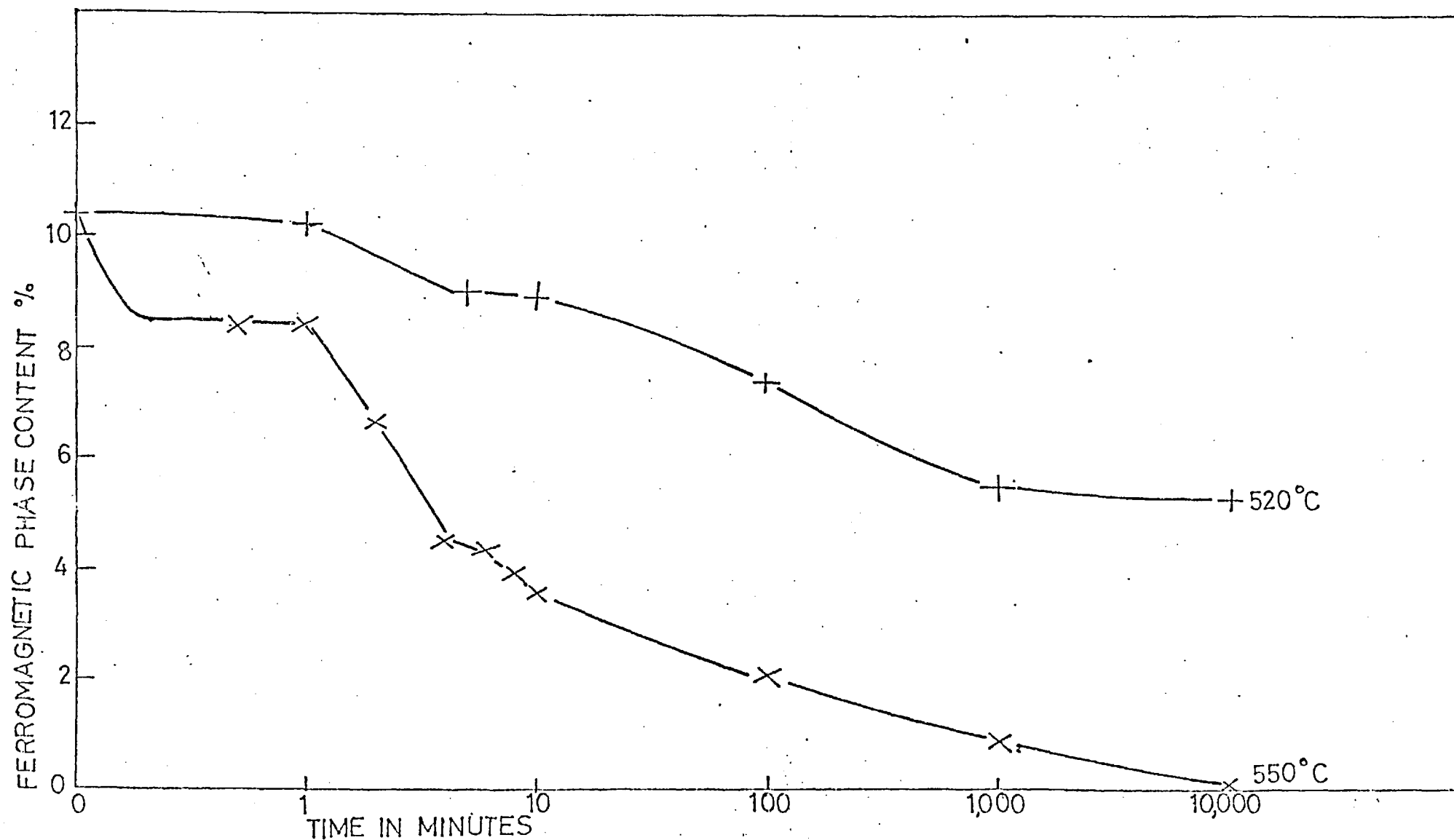


Fig. 3.4. Alloy A. Changes in ferromagnetic phase content on isothermal treatment of specimens deformed 50% at room temperature.

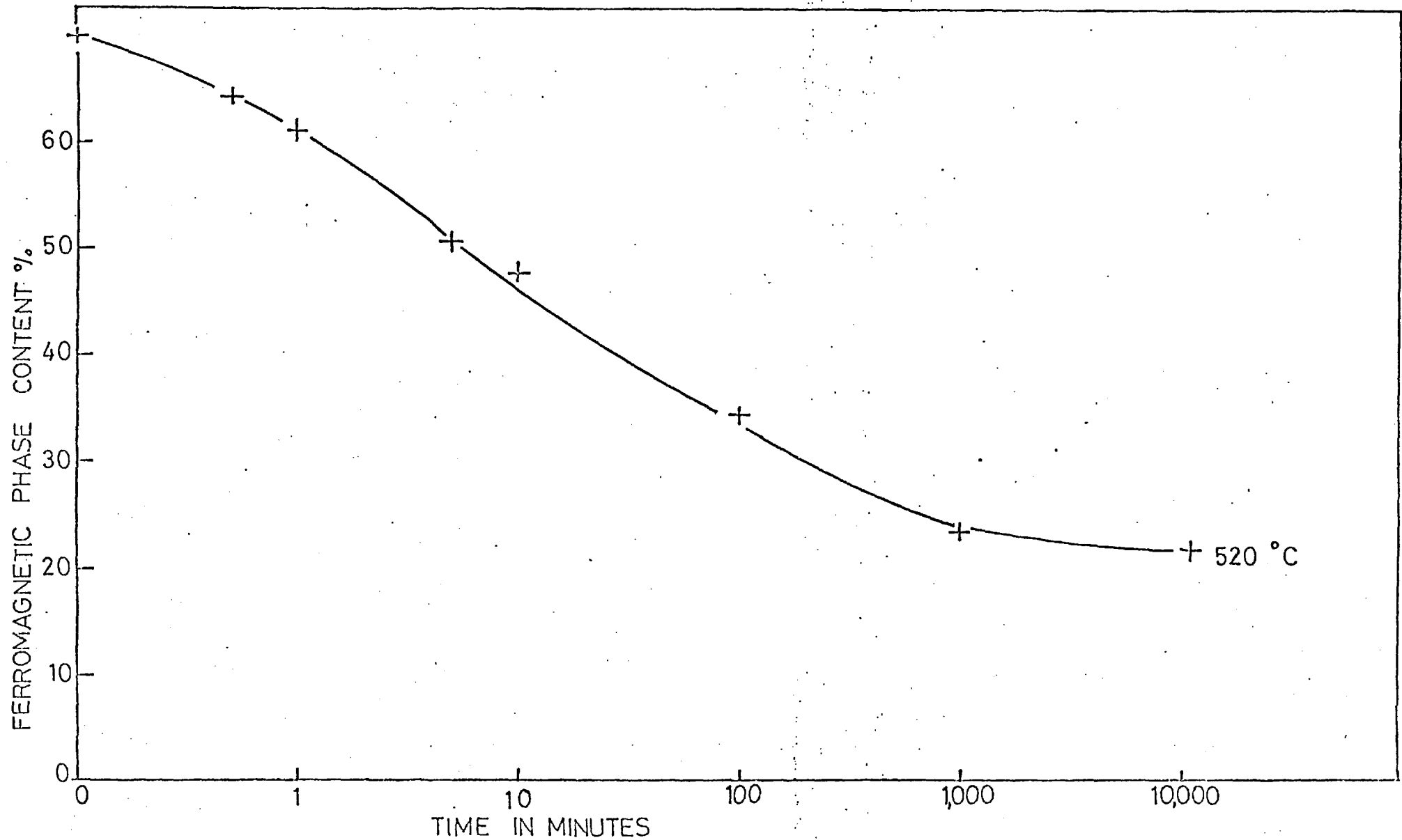


fig.3.5. Alloy A. Changes in ferromagnetic phase content on isothermal treatment of specimens deformed 50% at -78°C.

final amount probably depended on the initial amount of martensite present. Fig. 3.6 shows the relationship of the final amount of stable magnetic phase to the initial martensite content for isothermal transformation at 520°C i.e. at a temperature below that at which reactions one and two occurred. The relationship was non-linear, the increase in the stable magnetic phase per percentage increase in initial martensite decreasing as the martensite content increased.

The second difference between deformation-induced martensite and quench-induced martensite was that the third reaction began earlier in the deformed structure. This earlier development of reaction three made it difficult to detect reaction two in deformed samples; however, there was some indication of it at 550°C in Fig. 3.4.

The stabilising effects of the isothermal transformation were further investigated by taking specimens after various times and temperatures of isothermal transformation, reverting them for one minute at 600°C , and then retesting them magnetically. The results for quench-induced martensite and deformation-induced martensite are shown in Figs. 3.7 and 3.8 respectively. The broken lines show the magnetic phase content before the final reversion to 600°C . It can be seen that the first two stages caused no stabilisation of the magnetic phase, full reversion being subsequently possible at 600°C within one minute. However, when the third stage began, a stable magnetic phase developed which would not revert within one minute at 600°C . This stabilised phase increased in amount with time until it reached a peak, and

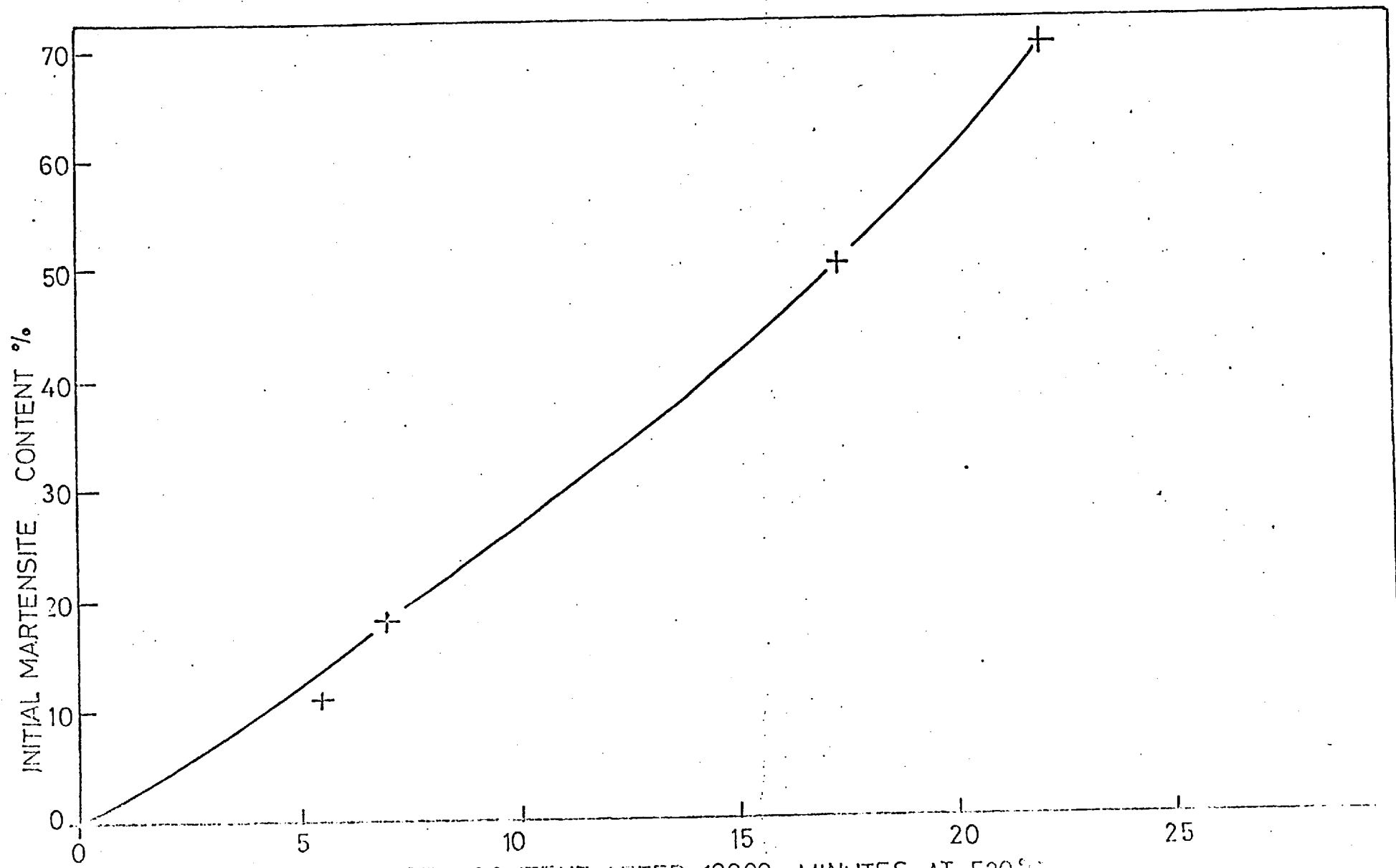


Fig. 3.6 Alloy A. The relationship between the ferromagnetic phase content after 10,000 minutes at 520°C and the initial martensite content.

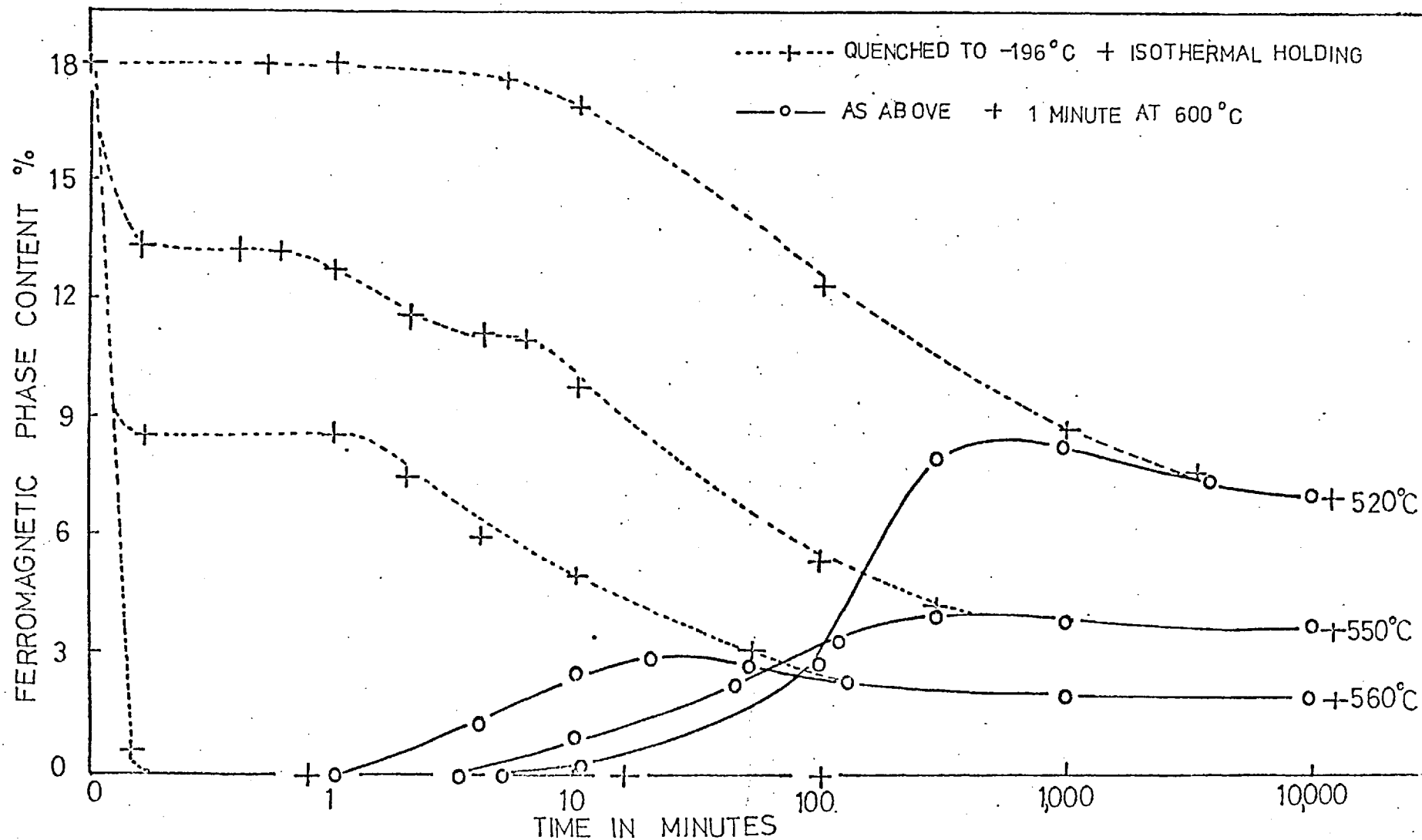


Fig. 3.7. Alloy A. The ferromagnetic phase content of quenched specimens after isothermal treatment + one minute at 600°C .

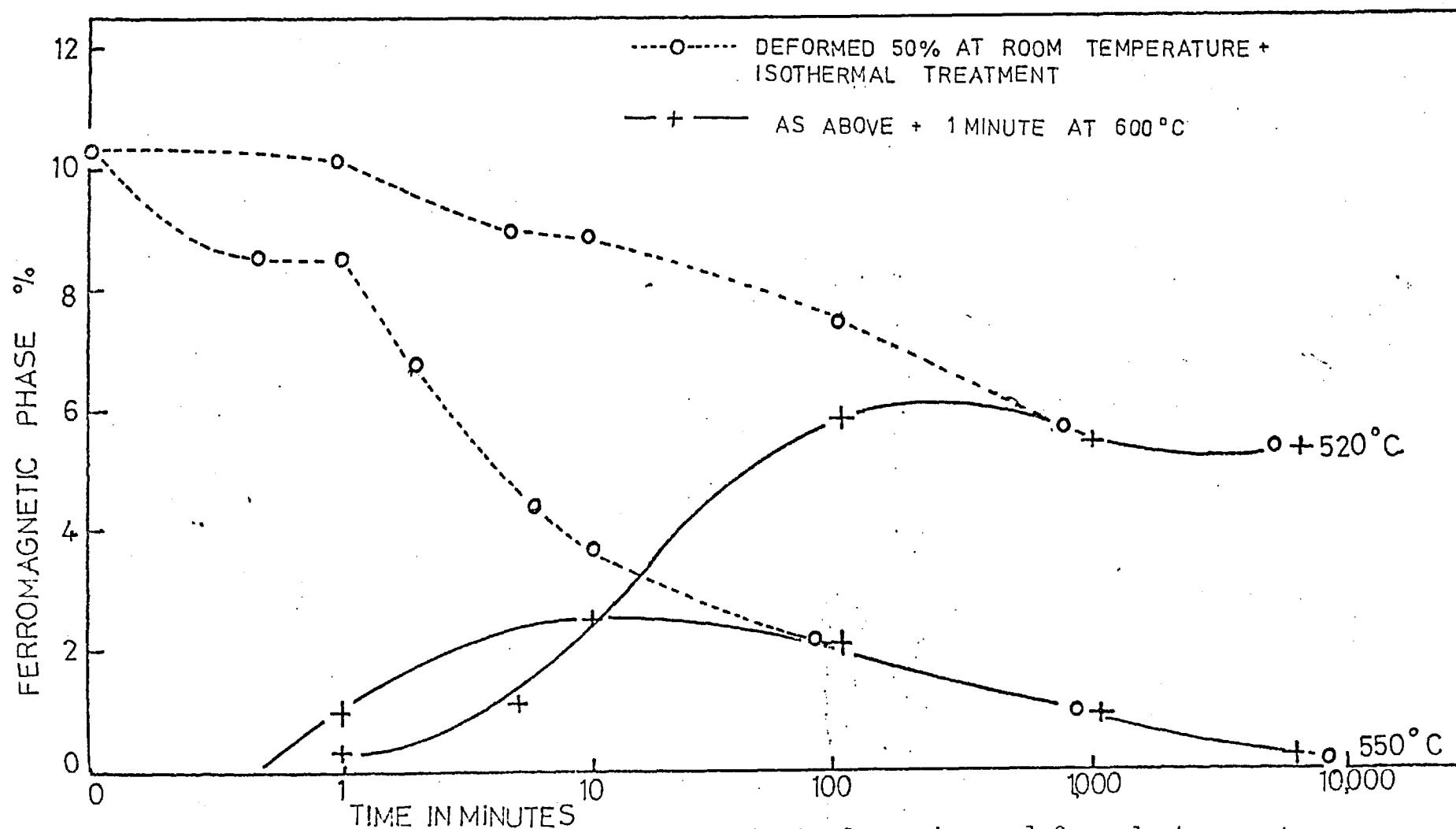


Fig. 3.8. Alloy A. The ferromagnetic phase content of specimens deformed at room temperature, isothermally treated and heated for one minute at 600°C.

then decreased somewhat before stabilising at its final amount. The formation of this stable phase can be seen to have begun earlier in deformed samples (Fig. 3.8) than in quenched samples (Fig. 3.7). Also it can be seen in Fig. 3.7, that the formation of this stable phase began earlier at higher temperatures, and that the starting point corresponded to the onset of stage three in the isothermal transformation. The initial rate of formation of the stable phase can be seen in Figs. 3.7 and 3.8 to have increased with increasing temperature.

In order to determine if the stabilisation of the magnetic phase involved a raising of the A_f , the experiment was repeated using 700°C instead of 600°C as the second reversion temperature. If the A_f had merely been raised some extra reversion at 700°C compared with 600°C might have been expected. The results are shown in Fig. 3.9. It can be seen by comparison with Fig. 3.7 that the higher reversion temperature made very little difference to the amount of the stable magnetic phase. However, when the specimens were held isothermally at 600°C, after an initial isothermal treatment at a lower temperature, the stable magnetic phase was found to decrease with increasing time, eventually being eliminated all together after a few hours.

In order to establish whether or not the stable magnetic phase could be induced without the presence of a prior martensitic structure, fully austenitic specimens were held isothermally at 530°C. Specimens of annealed austenite, reversed austenite, and austenite which had been warm worked 50% at 150°C in order to produce a dislocated

austenite, were used. In no case was any magnetic phase detected after three months at 530°C. Thus it was concluded that the presence of martensite was necessary for the nucleation of the stable magnetic phase.

The temperature dependence of the final amount of stable magnetic phase was investigated and the results are shown in Fig. 3.10. The broken line shows the amount of martensite present at the beginning of stage three of the transformation. It can be seen that the final amount of stable magnetic phase increased with decreasing temperature, (although the time required to form it increased with decreasing temperature), and that the amount relative to the initial martensite content also increased with decreasing temperature. The ratio of the martensite content at the start of stage three of the transformation to the final amount of stable magnetic phase after isothermal treatments is plotted against temperature in Fig. 3.11. The ratio was observed to increase gradually with increasing temperature, until the initial martensite content was reduced by stages one and two of the transformation, at which point the ratio increased dramatically. Thus the dependence of the stable magnetic phase on both temperature, and the initial martensite content, was illustrated.

3.1.2 Structural Aspects.

(i) Stages one and two of the transformation.

In order to study the effects of stage one of the transformation specimens reversed for one minute at 600°C were used. Light microscopy revealed very similar structures

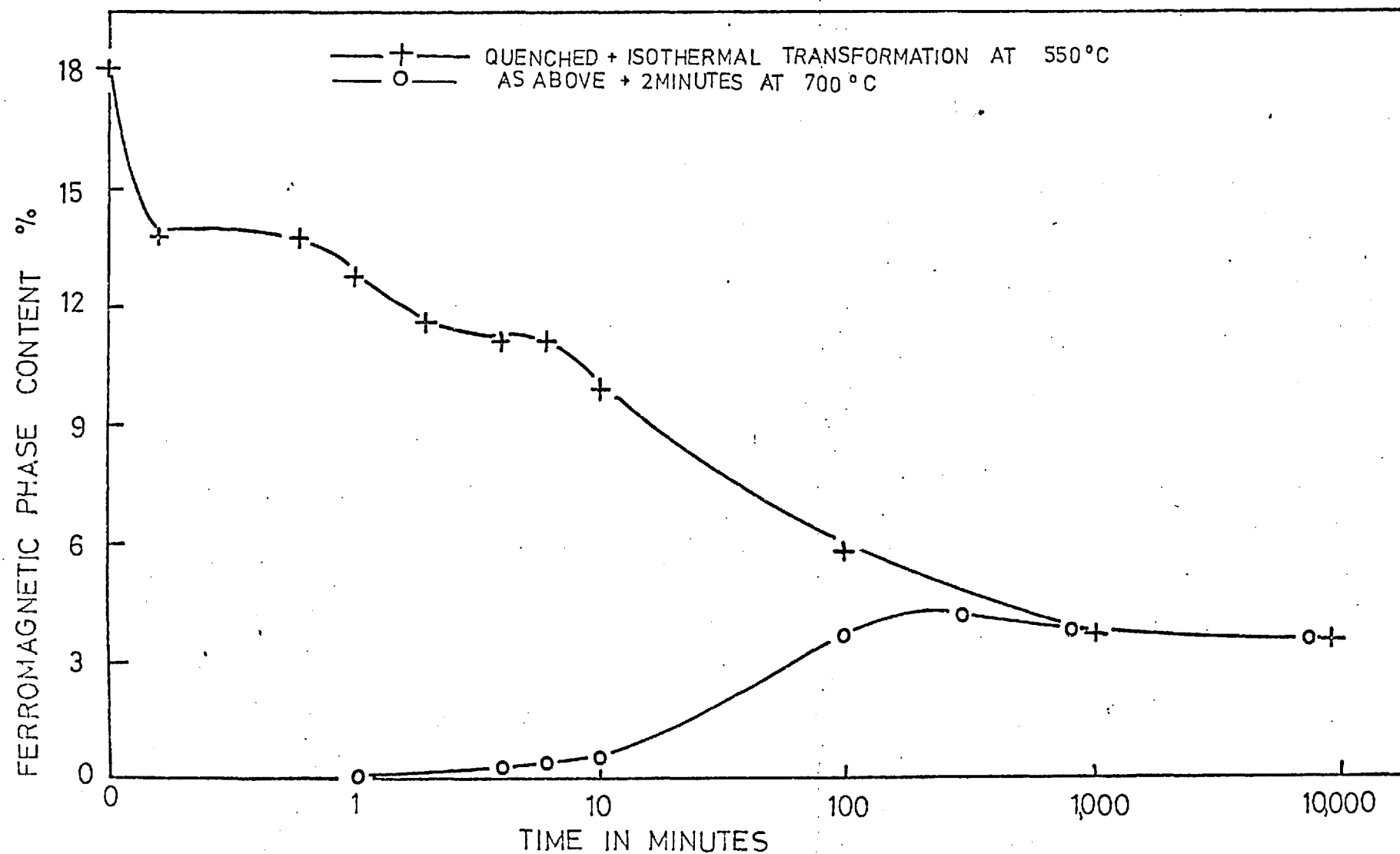


Fig. 3.9. Alloy A. The ferromagnetic phase content of quenched specimens after isothermal treatment + two minutes at 700°C.

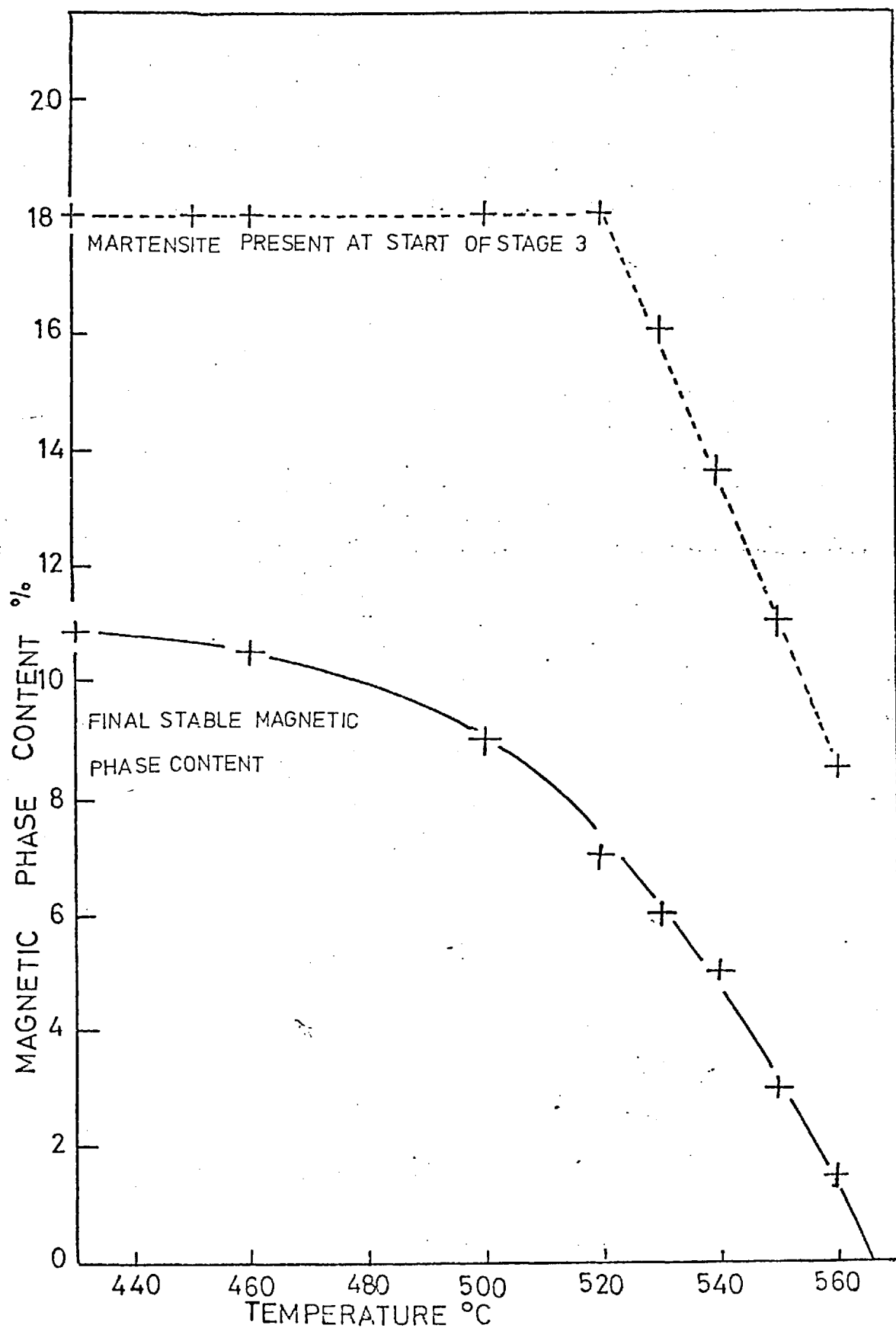


Fig. 3.10. Alloy A. The relationship between the martensite present at the start of stage three of the transformation and the final ferromagnetic phase content.

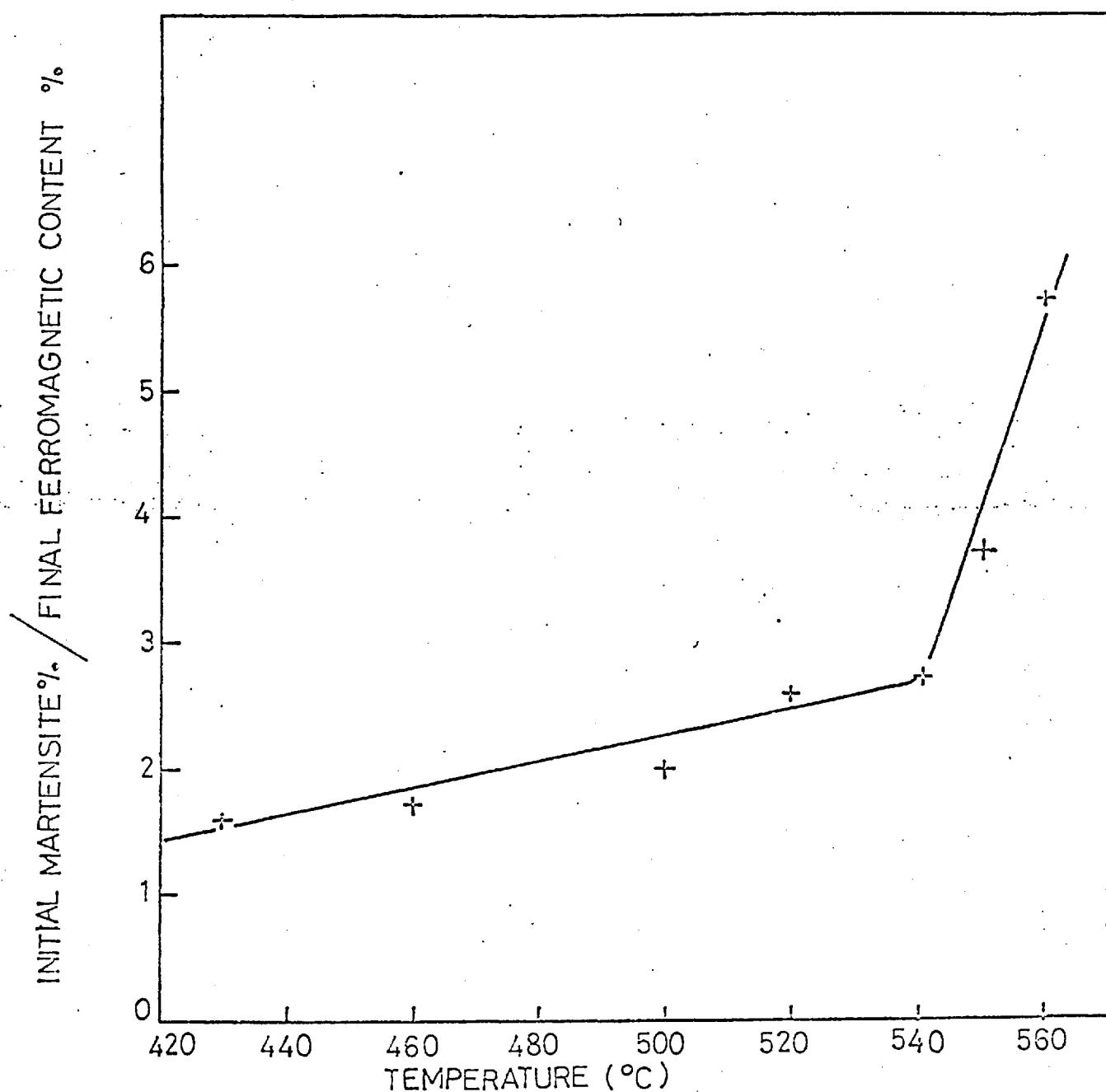


Fig. 3.11. Alloy A. The ratio of initial martensite content after quenching to the final ferromagnetic phase content after isothermal treatment at various temperatures.

in both quenched and reversed specimens. Fig. 3.12.1 shows a martensitic structure, and Fig. 3.12.2 shows a reversed austenite structure. The laths in Fig. 3.12.2 are generally termed 'ghost areas' and can be seen to have a similar morphology to the original martensite regions.

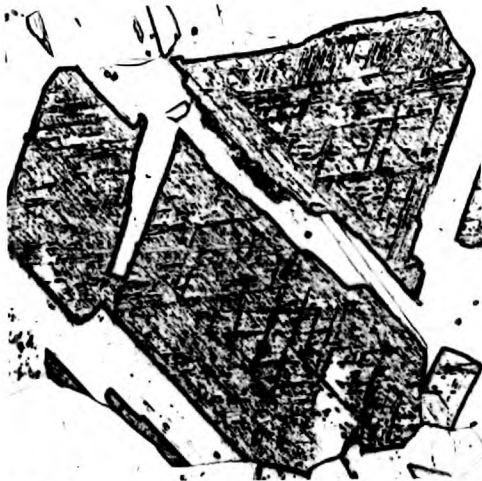
The electron microscope revealed the structure in greater detail as shown in Figs. 3.12.3 and 3.12.4. Fig. 3.12.3 shows a typical martensitic structure which has been well reported in previous literature^(1,8,58,68). The structure was one of laths containing many small grains of martensite with a high internal dislocation density. In between the grains of α' there were regions of ε and/or stacking fault clusters. The laths were surrounded by regions of retained austenite with a very low dislocation density. The reversed austenite in Fig. 3.12.4 can be seen to have been similar to the martensite in that there were individual, small grains of reversed austenite with a high, internal dislocation density, linked now by regions often containing a large number of very fine twins lying parallel to the long axis of the lath.

No changes in structure could be detected during the period of stage two of the transformation.

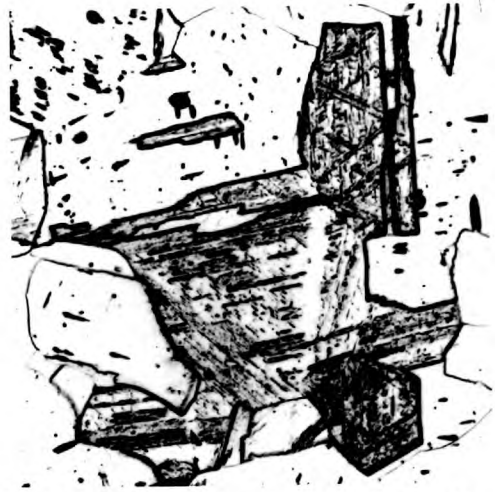
(ii) Stage three of the transformation.

The reaction was studied most easily at 520°C since this provided a large amount of martensite at the start of stage three, together with reasonably rapid formation of the stable magnetic phase. The initial structure was

Fig. 3.12



3.12.1. Alloy A. Quenched to -196°C x 200



3.12.2. Alloy A. Quenched to -196°C + 2 minutes at 600°C x 200



3.12.3. Alloy A. Quenched to -196°C



3.12.4. Alloy A. Quenched to -196°C + 2 minutes at 600°C .

martensite similar to that shown in Fig. 3.12.3. After 400 minutes at 520°C, when approximately 70% of the third reaction had been completed, the structure was as shown in Fig. 3.13.1. The former Σ areas appeared to be breaking up, possibly into small sub-grains, and the areas which were previously α' seemed to be forming irregularly shaped, but smooth sided grains. This structure continued developing until, when reaction three was completed after 10,000 minutes at 520°C, it appeared as shown in Fig. 3.13.2. The sub-grains formed from the Σ regions were often twin-related, and these regions no longer possessed a straight boundary with the retained austenite. The previously martensitic regions had formed into irregularly shaped grains, and Fig. 3.13.3. shows a diffraction pattern taken from one of these regions, the dark field micrograph associated with this pattern being shown in Fig. 3.13.4.

The diffraction pattern can be indexed as a $\{100\}$ b.c.c. pattern and this indicates that the new regions formed from the martensite were b.c.c. in structure. The amount of b.c.c. regions shown in Fig. 3.13.4 indicates that virtually all of the martensite grains in the lath had transformed into this product; the shape of the b.c.c. regions in Fig. 3.13.4 suggests that retransformation to austenite may have nucleated at the boundary between the α' grain and the Σ , and then the reversed austenite grown into the α' in an inhomogeneous manner.

Fig. 3.14.1 shows the structure at the completion of stage three of the transformation at 550°C. Fig. 3.14.2 shows the diffraction pattern taken from this area showing

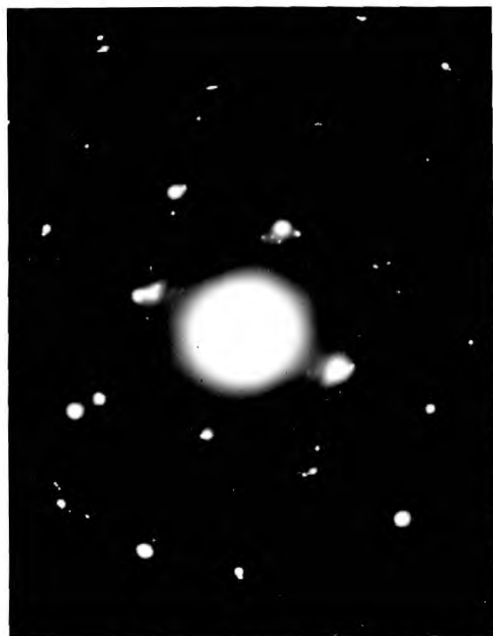
Fig. 3.13



3.13.1. Alloy A. Quenched to -196°C + 400 minutes at 520°C .



3.13.2. Alloy A. Quenched to -196°C + 10,000 minutes at 520°C .



3.13.3. Alloy A. Selected area diffraction pattern taken from 3.13.2. Basic (100) b.c.c. pattern.



3.13.4. Alloy A. Dark field micrograph taken using a b.c.c. reflection in 3.13.3.

a (110) χ pattern containing twin spots. Fig. 3,14,3 is a dark field micrograph taken from a twin spot. The upper lath in Fig. 3,14,1 appears broken up and contains numerous small grains, whereas the lower lath contains two relatively large grains. It seems possible, therefore, that the lower lath had reverted to austenite at stage one or two of the transformation, whilst the upper lath did not revert until stage three; and that stage three involved the breaking up of the lath into smaller grains. Fig. 3,14.4 shows a lath after completion of the transformation at 560°C; once again the sub-grain size was finer than in a lath of martensite.

In order to determine whether or not any diffusion was involved in reaction three, a specimen was taken after the completion of transformation at 520°C and examined with a microprobe analyser. The spot size of the analyser was too large (effectively 5 μm) for analysis of the b.c.c. regions to be possible. A scan of the surface however revealed a small variation in the nickel concentration within the specimen, although the scale of these variations was too fine for the instrument to associate them with any structural features.

3.1.3 Recovery.

It was mentioned previously that reversion at 600°C involved the formation of long, thin twins in the austenite regions between reversed austenite grains. In order to establish whether these twins were involved in the transformation itself, or were part of a recovery process, specimens were

Fig. 3.14



3.14.1. Alloy A. Quenched to -196°C + 100 minutes at 550°C .



3.14.2. Alloy A. Selected area diffraction pattern taken from 3.14.1. showing a basic (110) f.c.c. pattern



3.14.3. Alloy A. Dark field micrograph taken using a reflection in 3.14.2.



3.14.4. Alloy A. Quenched to -196°C + 100 minutes at 560°C .

examined after various isothermal heat treatments. It has already been observed in Fig. 3.14.1 that these twins were present after 1,000 minutes at 550°C; however, Fig. 3.15.1, taken after one minute at 550°C, shows that stacking faults were still present, whilst there was no evidence of the thin twins. It should be noted that, at this temperature, the ϵ should have reverted to γ (14), whilst the α' was not fully reverted. In Fig. 3.15.2 which shows the structure after 100 minutes at 520°C when no stage one nor two reaction would have occurred, the twinned structure can be clearly seen. The subsequent breaking up of these twinned regions into smaller lengths has already been seen in Figs. 3.13.1 and 3.13.2.

The formation of small, needle shaped grains was also noted in reversed δ regions and this is illustrated in Figs. 3.16.1 and 3.16.2. Twins (or stacking faults) are also evident in Fig. 3.16.1; therefore, the needle shaped grains do not appear to have formed from these. What seems to be a recrystallised grain also appears in Fig. 3.16.2 although such a feature was very rarely observed.

In order to study the recovery of reversed austenite under similar conditions, and to separate the recovery from the reverse martensite transformation, specimens were reversed for one minute at 600°C and then held isothermally at 550°C for 5,000 minutes. The structures developed are illustrated in Figs. 3.17.1 and 3.17.2. A heavily dislocated structure can still be detected in Fig. 3.17.2 but recrystallisation appears to have started. The long thin twins are evident in Fig. 3.17.1.

Fig. 3.15



3.15.1. Alloy A. Quenched to -196°C + 1 minute at 550°C .



3.15.2. Alloy A. Quenched to -196°C + 100 minutes at 520°C .

Fig. 3.16



3.16.1. Alloy A. Quenched to -196°C + 50 minutes at 550°C .



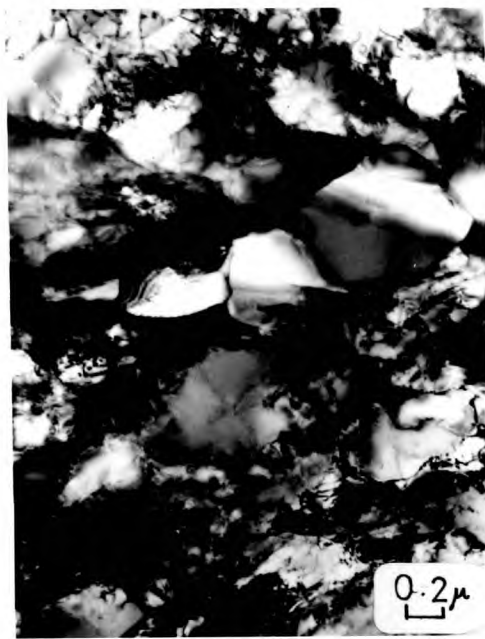
3.16.2. Alloy A. Quenched to -196°C + 100 minutes at 560°C .

In order to investigate the effect of a 'reversion' treatment on a dislocated austenite some specimens were warm worked approximately 40% at 150°C (ie above the M_d) and subsequently held for one minute at 600°C. The results are illustrated in Figs. 3.17.3 and 3.17.4. The long, thin twins were again in evidence, often forming in clusters as they did in reversed austenite. These twins were not present in the deformed structures (See Fig. 6.1.1). No recrystallised grains were observed. The overall dislocation density appeared somewhat less than that of reversed austenite.

Fig. 3.17



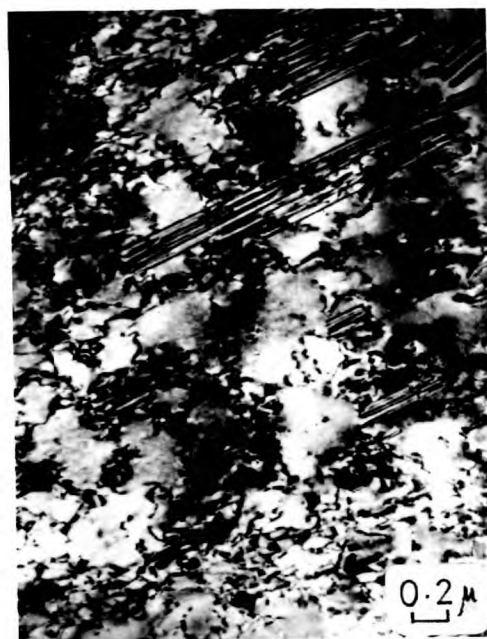
3.17.1. Alloy A. Quenched to -196°C + 1 minute at 600°C + 5.000 minutes at 550°C .



3.17.2. Alloy A. As 3.17.1.



3.17.3. Alloy A. Rolled 50% at $+150^{\circ}\text{C}$ + 1 minute at 600°C .



3.17.4. Alloy A. As 3.17.3.

3.2 DISCUSSION

3.2.1 Stage One of the transformation

This part of the transformation would appear to correspond to the martensitic reversion mechanism described for stainless steels by both Smith⁽¹⁾ and Breedis⁽⁵⁹⁾. The martensitic nature of the transformation is indicated firstly by the athermal manner of its occurrence and secondly by the surface tilting that it produced. Although it is possible to describe the transformation as a very rapid isothermal process, the dependence of the transformation on specimen size, and the fact that the times involved were of the order needed for the specimen to reach the temperature of the salt bath, make it much more likely that the reaction was athermal.

Further confirmations of the martensitic nature of this part of the transformation have been made by other workers with similar steels. Both Smith⁽¹⁾ and Breedis⁽⁵⁹⁾ have found that the transformation retraces the path of the direct transformation to martensite, the reversed austenite grains being in virtually the same orientation as the retained austenite around them. This indicates that, not only is it a shear transformation, but that the same variant of shear operates in both the direct and reverse transformations. Although the specific habit plane for the α/γ transformation in these stainless steels has not been determined, for crystallographic reversibility to occur it must be very close to that for the direct transformation. Kessler and Pitsch⁽⁴⁴⁾ found the habit planes for the direct and reverse

transformations in an Fe - Ni alloy to be very similar.

Since there is, therefore, evidence that the reaction was athermal, that the percentage transformation depended on the temperature, that a shape change was involved which produced surface tilting, and that it seems very probable that a habit plane could have been determined; terming the transformation 'martensitic', seems justified.

Since reaction one was not detected below 530°C it seems reasonable to define this temperature as the A_S for the reverse martensitic transformation. This is in contrast to Smith⁽¹⁾ who stated 450°C to be the A_S for the same alloy. However, if Smith's hardness, as opposed to magnetic results are used, then 530°C seems a better figure for the A_S . The earlier fall in magnetic phase content (at 450°C) found by Smith was probably not due to reversion but due to the formation of extra martensite on holding for two minutes below 450°C by a mechanism described by Mangonon and Thomas⁽⁶⁸⁾ involving thermally activated nucleation of martensite. This extra martensite did not form at temperatures above 450°C and so the impression of a decrease in martensite content was given.

The A_S and A_F were found to be unaffected by deformation of the α' . This is in confirmation of work by Smith⁽¹⁾ on a similar steel, but in contrast to work on Fe - Ni alloys^(49, 53) where plastic deformation has been found to raise the A_S . The structure of deformation-induced α' has been observed to be very similar to that of quench-induced α' in this alloy (see Fig. 6.1.1), and the reversion mechanism would appear to be the same. That the A_S and A_F appeared to be

unaffected by the strengthening of the retained austenite by deformation, is consistent with the observation of very little deformation of the retained austenite during the direct or reverse transformations. Golovchiner⁽³⁴⁾ found that, in an Fe - Ni - Ti alloy, deformation of the α' disturbed the interface and changed the reversion mechanism. This does not seem to have occurred in the present alloy. This may be due to the different type of martensite in the two alloys. The usual reason given for the lowering of M_s and raising of A_s by deformation⁽⁸⁴⁾ is that the strain energy associated with the transformation is increased. The different internal structures of the martensites in Fe - Ni alloys (twinned α') and Fe - Cr - Ni alloys (internally dislocated α') may mean that the strain energy required for reversion is not so markedly increased in Fe - Cr - Ni alloys by the dislocations introduced by deformation.

The decrease in hardness which occurred during this first part of the reversion can be attributed to several factors. Firstly, the f.c.c. structure is inherently weaker than the b.c.c structure due to the lower Peierls - Nabarro stress and the larger number of slip systems. Secondly, the misorientation between the reversed austenite crystals is very much lower than that between martensite crystals, and also the misorientations between the reversed austenite and retained austenite are less than those between martensite and retained austenite. As regards the dislocation density, it has been observed to be high in both martensite and reversed austenite crystals but no quantitative measurements have been possible. It seems likely that the reversed

austenite may have undergone some recovery at reversion temperatures.

There are conflicting views on whether or not reversed austenite inherits the defect structure of the martensite. Zaytsev and Gorbach⁽⁵⁷⁾ found that the defect structure was inherited; whereas Harvey⁽⁸¹⁾ found that a martensitic transformation 'swept out' the previous defect structure, a new defect structure being formed from the transformation shear stresses and the volume changes involved. The current work throws very little light on this question.

3.2.2 Stage two of the transformation

The isothermal characteristics of this part of the transformation are clear from Fig. 3.1. The transformation occurred over a fairly short time period and involved a decrease in the martensite content. Two possibilities present themselves as explanations of this stage of the transformation; firstly it may have been an isothermal martensitic reaction similar to that found in the direct transformation; or it may have been a diffusionally controlled transformation.

The fact that this stage of the transformation did not result in any raising of the A_f , i.e. the specimens reverted within one minute at 600°C, suggested that it was an isothermal martensitic transformation, since stage 3, which is thought to have been a diffusion controlled transformation, resulted in some stabilisation. The small, but consistent plateau in Fig. 3.1 between stages two and three of the transformation, argues against stage two being the initial

part of stage three in which not enough diffusion had occurred to produce stabilisation. It is difficult to conceive of a diffusion-controlled process reaching completion in as short a time as does stage 2, when stage three takes so much longer to reach completion.

The fact that stage two was not detected at 520°C whereas stage three was very much in evidence, also indicates that stage two was not linked with stage three; and thus that it was an isothermal, martensitic reaction. This also suggests that some athermal transformation needed to have occurred before stage two would begin. This fact can be explained by certain mechanisms of nucleation of an isothermal, martensitic transformation (dealt with later in this section) but it is difficult to see why a diffusional process should require some athermal reversion to nucleate it.

Another reason for concluding that reaction two was a martensitic transformation similar to stage one is that the hardness decrease per percentage decrease in magnetic phase content was very similar to that for stage one, whereas the decreases for both stage one and two were approximately twice that for stage three. The slightly lower value for stage two as compared with stage one may have been due to there having been more time in stage two for some recovery to have occurred. The hardness decrease accompanying stage three will be discussed later.

The structure of specimens after stage two was found to be very similar to that after stage one; nothing conclusive can be deduced from this observation. However, the

relatively short times involved allowed very little time for any structural changes to be produced by diffusional processes.

Thus, it is concluded that stage two was probably an isothermal, martensitic transformation. The fact that it occurred much faster than do isothermal transformations in the direct transformation to martensite can be attributed to the higher temperatures involved, resulting in greater thermal activation.

There appear to be three possibilities for the mechanism by which the isothermal martensitic transformation may have occurred. These are:

- 1) Relaxation of the stresses produced by both direct, and partial reverse transformations, may have removed some of the barriers to further transformation, i.e. the strength of the surrounding matrix was reduced thus reducing any mechanical stabilisation, and/or the strength of the α' was reduced, thus allowing the easier passage of an interface through it.

This mechanism may contribute to the overall transformation; however one objection to it is that there was no evidence that either the direct or reverse transformations caused any substantial deformation of the surrounding austenite.

Also the fact that the A_s and A_f were unaffected by deformation indicates that the reverse transformation was not affected by the strength of the martensite.

- 2) If some, but not all, of the α' grains in a lath reverted athermally, this may have introduced extra deformation into

the remaining α' grains, thus making them more unstable and causing them to revert isothermally. Alternatively if a reverted grain lay adjacent to an unreverted grain, it may have enhanced nucleation of the reverse transformation at the boundary.

The first alternative is unlikely, again since deformation of the martensite did not affect the A_s and A_f . The second alternative is more likely however, since workers with Fe - Ni alloys have found that reversion nucleates at the α'/γ boundaries. If one of a pair of adjacent α' grains reverted there must have been a change in the conditions at the boundary due to the shear transformation, and this may have caused later reversion to austenite under the influence of thermal activation.

3) Just as partial reversion of a lath may have affected the rest of the lath, so reversion of one lath may have affected laths lying adjacent to it. Thus, deformation of the remaining laths or a change in the boundary conditions may have caused subsequent, thermally activated, nucleation of the reverse transformation.

Once again the interface mechanism seems the more likely and, since the formation of sets of adjacent laths obviously assisted in the accommodation of the shears in the direct transformation, it seems likely that it would also be favoured in the reverse transformation. In support of this mechanism of transformation, as opposed to mechanism (2) above, is the fact that no partially-reverted laths were detected; however no conclusive evidence was obtained on this point. The interface mechanism is again in accord with

the findings of the workers on Fe - Ni alloys that reversion begins at the α'/γ interface.

3.2.3 Stage three of the transformation.

There appear to be three possibilities for the processes occurring during this part of the transformation. Firstly, some annealing out of defects would be expected at these temperatures and times. These recovery processes undoubtedly occurred but they offer no explanation of the decrease in magnetic phase content. Secondly, a thermally activated reversion process similar to that discussed for stage two could have taken place. Such a process, however, offers no obvious explanation of the stabilisation of the magnetic phase so that it would not revert fully at 600°C or 700°C. Thirdly, the reaction may have involved some form of diffusion control.

The first clear observation that emerges from the graphs in Fig. 3.1 is that the magnetic phase content decreased with time, i.e. the martensite transformed to a non-magnetic phase, presumably austenite. This transformation could have occurred either by an isothermal martensitic or by a diffusional process. The observation that the transformation occurred faster in deformation-induced martensite than in quench-induced martensite is more consistent with a diffusional than a martensitic process. This is because martensitic processes have generally been observed⁽⁸⁴⁾ to occur less readily in stronger matrices due to the increased strain energy involved in the transformation. Diffusional

processes, however, generally occur faster when a high dislocation density is present.

The second point to emerge from Fig. 3.1 and Fig. 3.7 is that, over a certain period of time, a stable magnetic phase was formed which would not revert martensitically to austenite at 600°C or 700°C. This stable phase has been identified by electron diffraction as being b.c.c in structure. This strongly suggests that it was ferrite.

According to reported phase diagrams⁽¹²⁰⁾ (see Fig. 3.18) the alloy composition lay very close to the $\delta / \alpha + \gamma$ phase boundary at these temperatures. Thus, it is possible that equilibrium ferrite may have formed, in small quantities, at least at the lower temperatures involved in this investigation. The composition of equilibrium ferrite would be much lower in nickel than the alloy composition. Thus, if the transformation was martensite $\rightarrow$ ferrite + austenite in equilibrium, the ferrite would be lower in nickel than the austenite. The microprobe analysis indicated some variation in nickel content over the specimen after isothermal transformation at 520°C, which is consistent with the possibility that a low nickel ferrite had formed.

One observation which is not in accord with the possibility that an equilibrium ferrite formed, is that the amount of the stable phase formed at any temperature depended on the initial martensite content. If the final structure had been at equilibrium, a standard amount of ferrite should have been present at a given temperature. The only way of reconciling this observation with the formation of equilibrium ferrite is if the equilibrium amount of

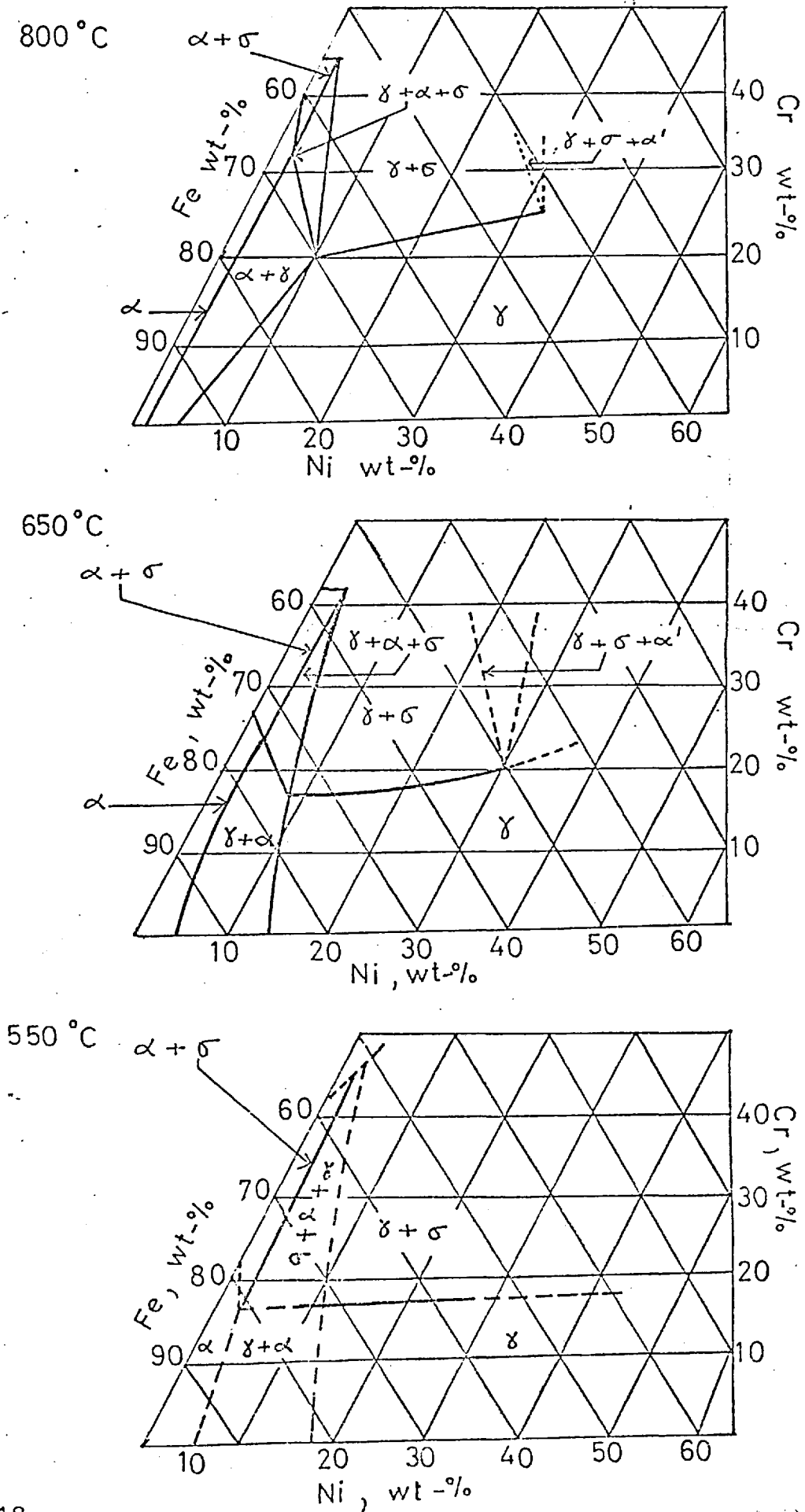


Fig. 3.18.

Isothermal sections of the Fe-rich corner of the Fe - Cr - Ni system (Cook and Brown(121))

ferrite were greater than, or equal to, the largest amount of ferrite recorded i.e. 22% at 520°C. Then, since transformation only occurred in martensitic areas, it is possible to understand the lower amounts of ferrite produced from the lower martensite content specimens. 22% ferrite at 520°C, however, is much more than the equilibrium amount indicated by the phase diagram.

The possibility that the slow transformation of $\gamma \rightarrow \alpha$ at low temperatures has resulted in unreliable phase diagrams is pointed out in the work of Zakharov et al⁽⁵⁶⁾. They calculated that an Fe - 30% Ni alloy should contain 27% α in equilibrium at 400°C. They could induce no α to form in an austenitic structure held at 400°C for 800 hours, but, by quenching to form α' , and then holding at 400°C, the equilibrium 27% α was formed within 6 hours. In the work of Cook & Brown⁽¹²⁾, however, some deformation-induced martensite was formed before equilibration and so the phase diagram that they produced should not be particularly prone to this error.

Another possibility is that nickel diffusion out of the martensite resulted in the composition in these regions moving into the two-phase region. The martensite and austenite before transformation began were of the same composition and therefore, if the alloy was in the single phase, austenitic region, no long range diffusion would have been necessary for the martensite $\rightarrow$ austenite transformation. However, whilst this transformation was proceeding, a b.c.c phase was present which was much higher in nickel content than the equilibrium nickel content for

a b.c.c phase at the temperature involved. Therefore, nickel may have diffused out of the martensite, resulting in the composition in the martensitic regions moving into the two-phase region and the consequent formation of a stable ferrite. Diffusion in austenite is much slower than in ferrite, and, at these temperatures, diffusion in the austenite would have been too slow to allow the attainment of final equilibrium once a low-nickel ferrite had formed. This type of mechanism is consistent with the dependence of the final amount of ferrite on the initial martensite content since a larger number of martensite regions initially would have resulted in a larger number of two-phase regions after transformation.

The temperature dependence of the final amount of ferrite may have been due to the movement of the $\alpha + \gamma / \gamma$ phase boundary to slightly higher nickel levels with decreasing temperature. Also the kinetics of the $\alpha' \rightarrow \gamma$ transformation may have been reduced more by decreasing temperature than was the diffusion rate of nickel, resulting in more nickel diffusion occurring per percent transformation.

The activation energy for stage three of the transformation was calculated by plotting the time to 50% transformation against the reciprocal of the absolute temperature, Fig. 3.19. The point for 560°C fell below the straight line drawn, probably due to some stage two transformation having occurred during the initial part of stage three. The calculated value for the activation energy was 59.7 Kcals/mole. This figure was not very accurate due to the small temperature range and small number of points

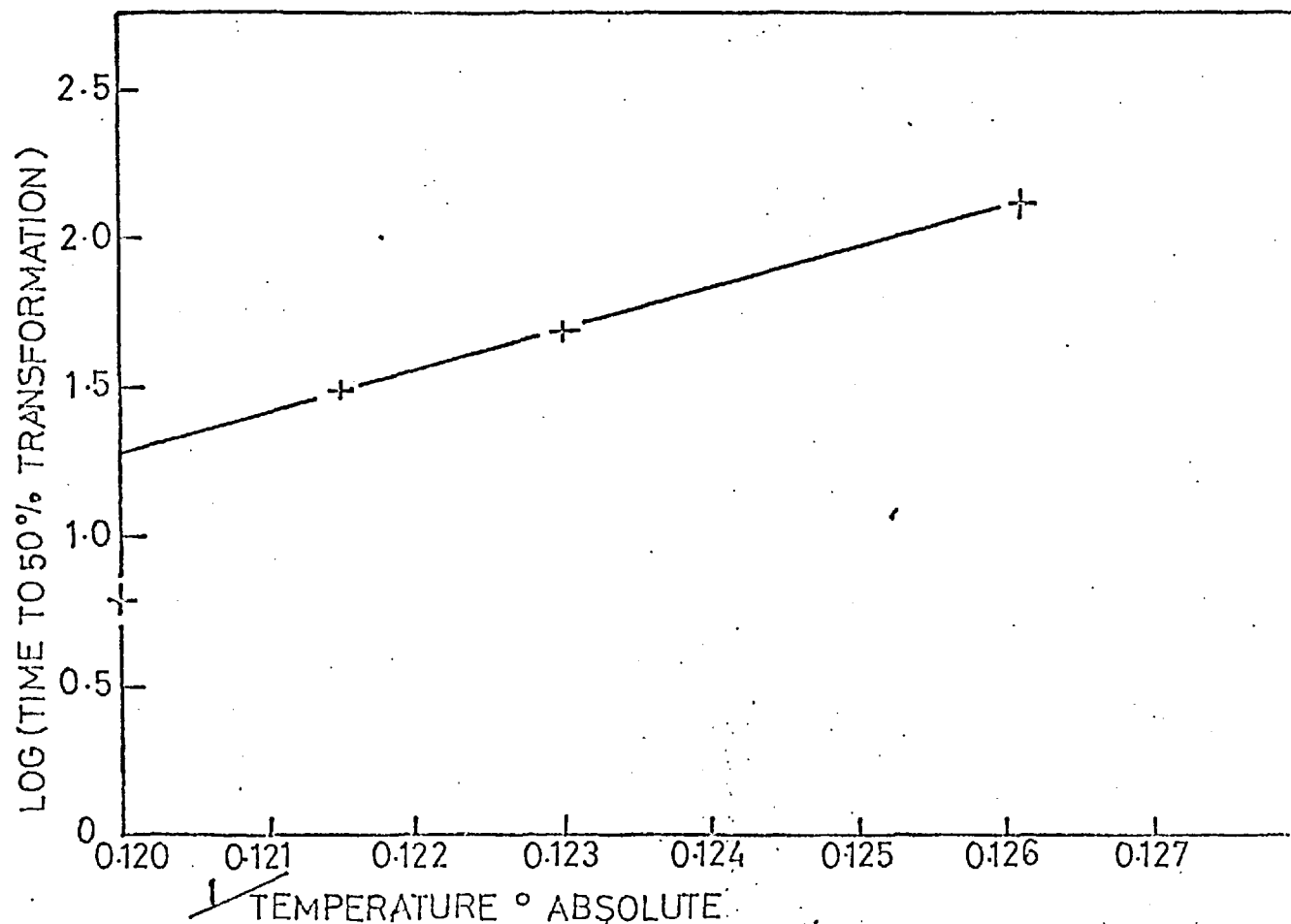


Fig. 3.19. Alloy A.

Arrhenius plot of log (time to 50% transformation) against the reciprocal of the absolute temperature for stage three of the transformation.

used, but it compares well with the figure of 58.7 Kcals/mole quoted by Hirano et al⁽⁸⁹⁾ for the diffusion of nickel in ferromagnetic α - iron. This lends support to the suggestion that nickel diffusion was involved in the transformation.

Krauss and Cohen⁽⁴⁶⁾, Kessler and Pitsch⁽⁴⁴⁾, and Zel'dovitch and Sadovskiy⁽⁸⁰⁾, have all postulated that nickel diffusion occurs across the α'/γ interface on isothermally holding partially martensitic iron-nickel alloys between A_s and A_f .

One other possible explanation of the formation of the stable magnetic phase is that, as the $\alpha' \rightarrow \gamma$ transformation proceeded, recovery took place in the α' . The removal of defects from the α' by recovery would have lowered the free energy of the martensite phase and resulted in some degree of stabilisation with respect to austenite. This stabilisation may have been sufficient, eventually, to slow down the kinetics of the $\alpha' \rightarrow \gamma$ transformation and to effectively stop it. Even if one of the other suggested mechanisms applied, recovery probably contributed to some degree to the stabilisation. One fact which is inconsistent with stabilisation due to recovery is that raising the reversion temperature to 700°C had little effect on the stabilisation. If recovery was raising the A_f it would be expected to be a gradual process and some difference in reversion would be expected to be noticeable at 700°C.

If one of the diffusional mechanisms applied then, presumably, diffusion in the austenite was possible at 600°C and the ferrite reverted to equilibrium austenite by a diffusional process. This means that the $\gamma/\alpha + \gamma$

phase boundary was below 600°C . If the recovery mechanism applied then the kinetics of the reverse transformation must have become fast enough at 600°C for it to proceed.

Another feature requiring explanation is the decrease in magnetic phase content after the point at which no magnetic phase would revert within one minute at 600°C (see Figs. 3.7, 3.8 and 3.9). This may have resulted from an attempt to reach equilibrium, but, if this was so, it is again difficult to understand why a standard amount of ferrite was not formed at a given temperature. If a low nickel ferrite had formed, it seems that full stabilisation of the martensitic reverse transformation occurred before the ferrite reached a fully stable form. This is not unreasonable since more superheating is required to make ferrite revert martensitically than diffusionally⁽³²⁾. If the recovery mechanism had operated then, since a martensitic reaction requires a greater driving force than a diffusional reaction, it is reasonable that martensitic reversion is stopped by recovery earlier than diffusional reversion.

One other observation requiring explanation is that the fall in hardness per percentage loss of ferromagnetic phase was less during stage three than during stages one and two. In terms of recovery processes the opposite effect would be expected since the time available for annealing out of defects was much longer during stage three. One possibility for this effect is that, during stages one and two, the martensite reverted to austenite of virtually the same orientation as the retained austenite, thus, the boundaries between reversed and retained austenite were low

angle as compared with the high angle boundaries around the martensite. It also seems likely that, during the first two stages, whole laths reverted at a time. During stage three, however, the boundary probably moved slowly, and thus, whilst in stage one a whole lath may have reverted for the same loss of martensite in stage three several laths would have reverted partially. Thus, a larger number of b.c.c particles would have been left in stage three resulting in greater strengthening.

The current work appears to correlate quite well with Smith's dilatometry results at varying heating rates⁽¹⁾. At 'slow' heating rates Smith suggested that a diffusion controlled reversion process began at 450°C. This seems confirmed by the present results and the formation of some stable ferrite probably occurred as well. At a 'medium' heating rate Smith also postulated a diffusional process beginning at 520°C; this may have involved some isothermal martensitic reversion as well as some diffusional transformation. At 'fast' heating rates reversion was clearly martensitic.

Although the present work correlates well with that of Smith on a very similar alloy, neither this nor Smith's work agrees with that of Breedis⁽⁵⁹⁾ who found no change in the magnetic content of an Fe - 16Cr - 12 Ni alloy annealed for two minutes or two hours at temperatures between the A_s and A_f . No explanation can be suggested for this anomaly.

3.2.4 Recovery and Recrystallisation.

There has been some discussion⁽¹⁾ as to whether the

twins and small stacking faults observed after reversion in stainless steels were associated with the transformation itself or formed part of recovery processes. These structures appeared in regions which were formally ϵ or stacking faults in the partially martensitic structure, and sometimes passed through reversed austenite grains. ϵ in this alloy has been found to be fully reverted within fifteen minutes at 400°C ⁽¹⁷⁾; however, Fig. 3.15.1 shows that twins were not always present after reversion for 1 minute at 550°C although stacking faults were still present. Thus, either the ϵ did not revert athermally and was still present in Fig. 3.15.1, or the twins were not associated with the reversion of ϵ to γ . The ϵ structures had certainly disappeared within 1 minute at 600°C being replaced by the twins and small stacking faults - see Fig. 3.15.4.

The possibility that the twins were associated with the athermal reversion of α' to γ appears to be refuted by Fig. 3.15.2 which shows twins to have been present after isothermal holding for 100 minutes at 520°C at which temperature no martensitic reversion of α' to γ had occurred. Thus, twins have been observed both when no stage 1 transformation (Fig. 3.15.2), and no stage 3 transformation (Fig. 3.15.4), had taken place. The fact that similar twins were observed in warm worked structures after a 'reversion' heat treatment, when no α' had been present originally (Figs 3.17.3 and 3.17.4) adds further weight to the conclusion that the twins were not associated with reversion of α' .

Thus, the possibilities remain that the twins formed part of the reversion of ϵ possibly occurring isothermally

below 600°C , or, that they were formed by recovery processes after the ϵ had reverted. ϵ can be considered as a γ structure faulted on every other $(111)_{\gamma}$ plane⁽⁹⁰⁾. Thus, the f.c.c. stacking sequence ABCABC, faulted on every other plane becomes ACACAC. If, then, it is assumed that reversion of ϵ also involved faulting on every other plane it is possible to obtain either ABCABC again, or, CBACBA which is the stacking sequence of a twin in an f.c.c. structure. Thus it is possible to envisage the reversion of ϵ to γ producing twinned γ by the same sort of mechanism as that which produced the initial ϵ . The faulting on alternate $\{111\}$ planes described above can be accomplished by the movement of $\frac{a}{6}\langle 112 \rangle$, Shockley partial dislocations as proposed by Christian⁽⁹⁰⁾. For each set of $\{111\}$ planes there are three possible $\frac{a}{6}\langle 112 \rangle$ shears, and Kotval and Honeycombe⁽⁹¹⁾, working on the f.c.c. to h.c.p transformation in Cu - Ge, found that all three operated in the thermally activated formation of the h.c.p. phase, thus producing regions of ϵ which showed surface tilting within them. They propose that the transformation can be explained in terms of the pole mechanism propounded for the f.c.c h.c.p transformation in Cobalt by Seeger,⁽⁹²⁾.

Thus, it is possible to envisage the reverse transformation i.e. h.c.p $\rightarrow$ f.c.c. occurring in a similar sort of way. The large number of fine twins formed from an ϵ region may be considered as formed by different variants of the shear required, this process occurring presumably because it allows better accommodation of the shears involved. The actual mechanism may have been associated with the pole mechanism

proposed by Cottrell and Bilby⁽⁹³⁾ for the formation of a twin from a partial dislocation.

Kotval and Honeycombe⁽⁹¹⁾ proposed that some solute segregation to the stacking faults was necessary before the h.c.p phase would form, it then forming martensitically. Some similar mechanism in the present case could explain why the twins seemed to form isothermally at the lower temperatures.

The other possibility, that the twins form part of recovery, is supported by work on Fe - Ni alloys by Krauss⁽⁴⁵⁾ and Krauss and Cohen⁽⁴⁶⁾ who found that islands of twins formed about 50°C above the A_f . They suggested that these twins formed by the coalescence of high energy stacking faults which arose from irregularities in the reverse shear transformation. The driving force for this process was presumably that a twin fault has approximately one half of the energy of a stacking fault, due to half the number of nearest neighbour bond violations being involved. The mechanism could, once again be the Cottrell - Bilby pole mechanism. Since twins formed at temperatures below the A_s the stacking faults in the present case cannot have arisen from the reverse martensite transformation, but may have formed as a result of the reversion of ϵ , or may have been associated with the direct transformation.

Fig. 3.13.2 shows the structure of these previously ϵ regions after 10,000 minutes at 520°C. An intermediate structure after 400 minutes at 520°C is shown in Fig. 3.13.1. The length of these regions was obviously restricted by the α' and later the α grains, (compare these Figs. with

Fig. 3.17.3) and they appeared to break up into small polygonised grains, elongated in the long direction of the lath. These grains were often still twin-related to each other.

Polygonised grains were also apparent after shorter times at 550°C and 560°C as shown in Figs 3.16.1, 3.16.2 and 3.14.4. However, in Fig. 3.16.1 and 3.14.4. twinned regions were also apparent, and the polygonised grains may have been associated with a previously α' region.

The formation of these sub-grains was presumably due to recovery processes. Similar elongated sub-grains were found by Hu⁽⁹⁴⁾ in microband regions in an Fe - 3% Si alloy. These microbands were narrow regions, in between matrix deformation bands, which consisted of several narrow laths with $2-3^{\circ}$ misorientation between them and a high internal dislocation density. Hu found that recovery caused the formation of elongated sub-grains, and that recrystallisation subsequently occurred by a sub-grain coalescence mechanism.

Smith⁽¹⁾ found that recrystallisation of reversed austenite in these stainless steels at 850°C occurred by a continuous recovery process, or, recrystallisation 'in situ'. Figs. 3.16.2 and 3.17.2 show what appears to be the formation of small, recrystallised grains; these were very uncommon. Nevertheless it appears that recrystallisation may have proceeded more normally at these lower temperatures than at 850°C as described by Smith. It may be that recovery processes proceeded too fast at 850°C for recrystallised grains to be able to nucleate.

CHAPTER 4.

TRANSFORMATION CYCLING.

There has been considerable discussion^(1,33,35,43,46,48, 83,84) in the literature on the reason for the stabilisation of austenite which is produced by the presence of reversed austenite. This feature has been studied in the present work by means of dilatometry and optical and electron microscopy, including the use of a cooling stage in the electron microscope. The cooling stage was intended for use in studying the sites in which second generation martensite was produced, by observing the transformation to martensite under continuous cooling conditions. In the course of this work some observations were made of the formation of first generation martensite and these are also reported in this section.

4.1 RESULTS

4.1.1 Observations in the Cooling Stage.

The stage used liquid nitrogen as a coolant, and the specimens could be cooled to a minimum temperature of -150°C ; thus, since alloy A had a bulk M_s of -50°C it was hoped that martensite formation would be observed in the electron microscope. It was found, however, to be very difficult to produce any martensite in the regions of the foils which were thin enough to observe in the microscope, although optical microscopy, after cooling, revealed copious

surface tilting, indicating transformation to martensite, in the thicker regions around the edges of the disc specimens.

Nevertheless, some observations were made of structural changes in samples of alloy A under continuous cooling. Fig. 4.1 shows the structure of solution treated samples cooled to -100°C and -150°C . Although very little martensite was produced, a number of stacking faults were formed, e.g. Fig. 4.1.1 These stacking faults were not usually associated with any martensite, but occasionally they were linked with heavily dislocated regions as shown in Fig. 4.1.2. These dislocated regions did not show the morphology of the lath martensite observed in bulk material, but had a morphology similar to that described by Hull⁽¹⁰⁸⁾ for martensite produced in a thin foil of an iron-nickel alloy, and by Breedis⁽⁸⁾ for martensite produced in a thin foil of an 18/8 stainless steel.

Fig. 4.1.3 shows what appear to be martensite laths linked with regions of stacking faults or ϵ . The heavily dislocated regions described above were often found to grow by the slow movement of one of their boundaries, as did the regions described by Hull. Fig. 4.1.4 illustrates one of these regions in which the boundary running from left to right at the bottom of the micrograph was observed to move slowly downwards on further cooling of the specimen.

Fig. 4.2 shows the sideways growth of an initial martensite lath, under the influence of continuous cooling. The growth occurred partly by slow boundary migration and partly by 'bursting' as illustrated in the figure. The slow boundary migration was similar to that described above for

Fig. 4.1



4.1.1. Alloy A. Solution treated + cooled in the electron microscope to -150°C .



4.1.2. Alloy A.
As 4.1.1.



4.1.3. Alloy A.
As 4.1.1.

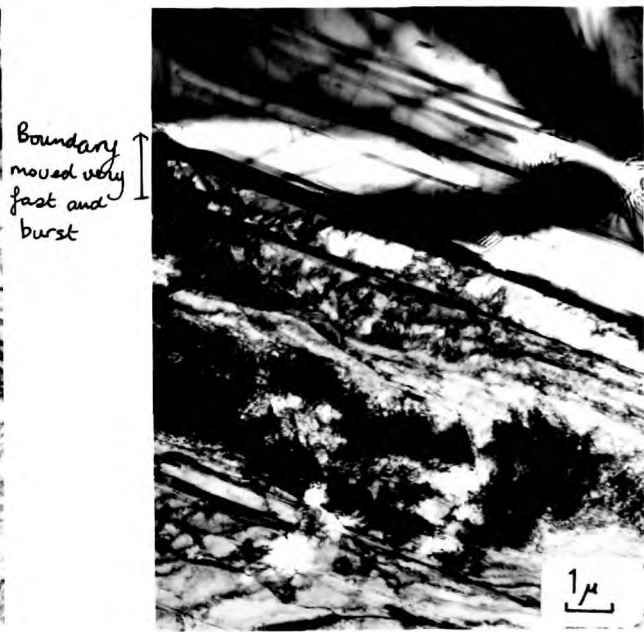


4.1.4. Alloy A. Solution treated + cooled in the electron microscope to -100°C .

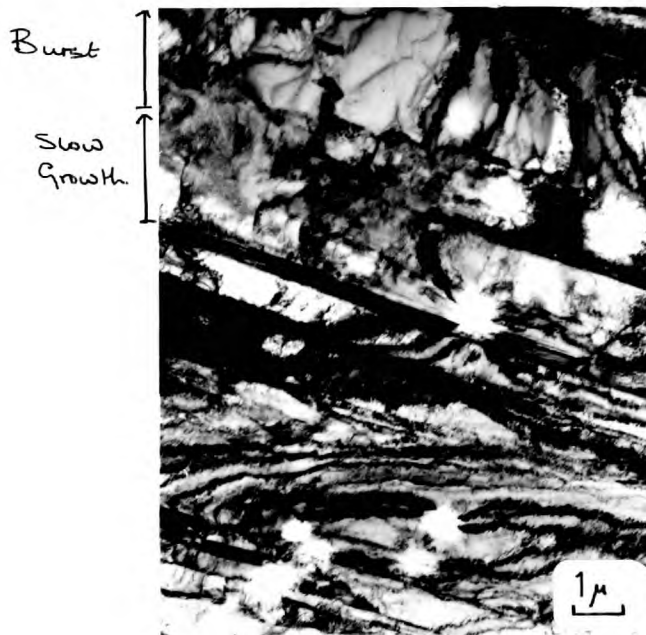
Fig. 4.2



4.2.1. Alloy A. Solution treated + cooled in the electron microscope to -70°C .



4.2.2. Alloy A. Same area as shown in 4.1.1. further cooled in the electron microscope to -100°C .



4.2.3. Alloy A. Same area as 4.1.1. and 4.1.2. further cooled in the electron microscope to -150°C .



4.2.4. Alloy A. Same specimen and treatment as 4.2.3. An area to the right of 4.2.3.

the heavily dislocated regions. Narrow stacking faults can be seen in Figs. 4.2.1 and 4.2.2 lying in front of the moving boundary and parallel to it. No similar stacking faults were observed in a room temperature examination of thin foils which had been prepared from material quenched to -196°C . Examination of the same areas in Fig. 4.2.3 reveals that these stacking faults seem to have disappeared during the course of the transformation to martensite. The small lath produced by bursting in Fig. 4.2.2 also appears to have generated some stacking faults at its boundary with the austenite. Fig. 4.2.4 shows a region, just to the right of that shown in Figs. 4.2.1 - 4.2.3, where the martensite laths met a prior austenite grain boundary. The impingement of the martensite on the boundary appears to have caused the generation of stacking faults in the austenite on the other side of the boundary,

The production of second generation martensite in the cooling stage was found to be even more difficult than that of first generation martensite, presumably due to the stabilisation of austenite by reversed austenite. Some observations were made, however, and are illustrated in Figs. 4.3 and 4.4. Fig. 4.3 shows structures in a foil cooled to -150°C . The two dark field micrographs were taken of the same area as the bright field micrograph using two different austenite reflections which were twin related. The interesting feature is the presence of stacking faults, labelled in Fig. 4.3.4, within the laths, running at various angles across the laths. Similar faults were not observed in quenched and reversed specimens examined at room temperature. Possibly,

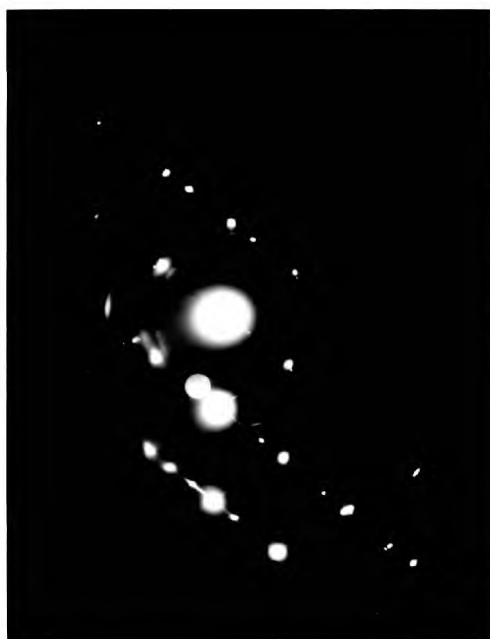
Fig. 4.3



4.3.1. Alloy A. Quenched to -196°C + 2 minutes at 600°C + cooled in the electron microscope to -150°C . Dark field micrograph taken using an austenite reflection from 4.3.3.



4.3.2. Alloy A. Same treatment and area as 4.3.1. Dark field micrograph taken using an austenite reflection in 4.3.3. twin related to the one used for 4.3.1.



4.3.3. Alloy A. Selected area diffraction pattern taken from 4.3.4. (110) austenite diffraction pattern showing twin spots with the twin axis on $[1\bar{1}1]$



4.3.4. Alloy A. Same treatment and area as 4.3.1. and 4.3.2. Bright field micrograph.

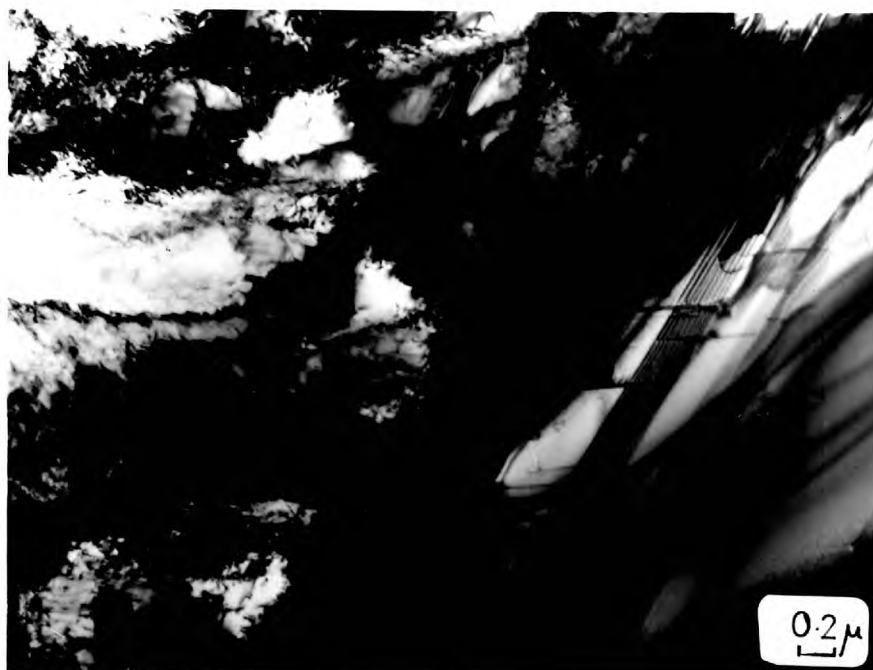
therefore, these faults may have been associated with the beginning of the formation of second generation martensite.

Fig. 4.4 shows two micrographs of the same area of a foil, initially containing 18% reversed austenite, after cooling to -60°C and -100°C respectively. The structure in the upper part of the micrographs does not have the characteristic reversed austenite structure (see Fig. 3.1.4) although it does contain a high dislocation density and has the appearance of the heavily dislocated regions, assumed to be martensitic, mentioned earlier. Below these dislocated regions in Fig. 4.4.1 is a region containing bands of stacking faults. In Fig. 4.4.2 this faulted region has been replaced by a band of martensite, although it is not of the characteristic lath structure (see Fig. 3.1.3). This martensite had clearly not formed in a region of reversed austenite, but one of retained austenite.

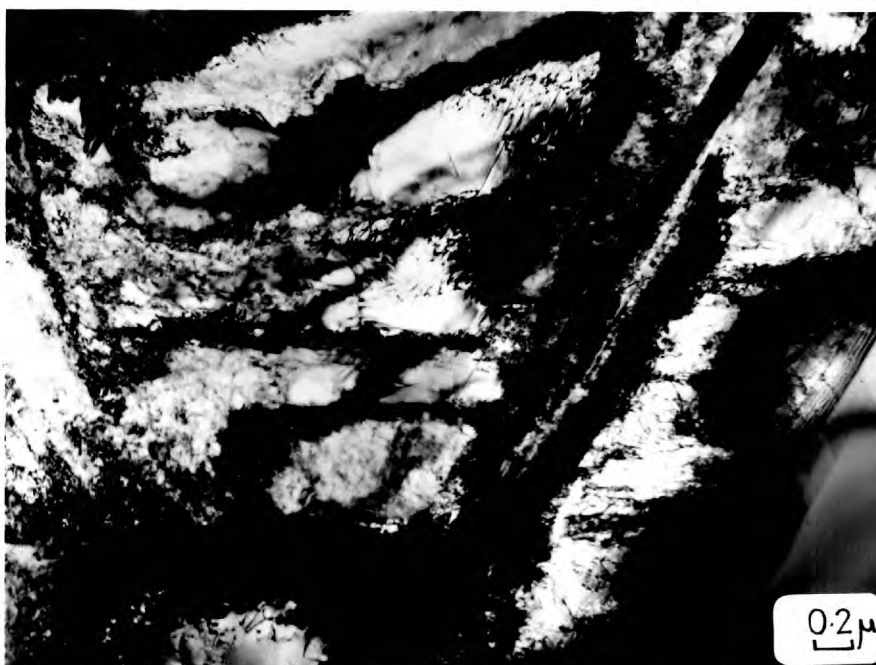
4.1.2 Further Metallographic Evidence.

Fig. 4.5 shows bright and dark field micrographs taken in a room temperature examination of a foil which had been quenched to -196°C , reversed for one minute at 600°C , and then re-quenched to -196°C . Fig. 4.5.3 shows the regions imaged from an austenite diffraction spot. Thus, it can be seen that the area was basically austenitic, and that the high dislocation density indicates that it was an area of reversed austenite. However, in the centre and top right hand corner of Fig. 4.5.1 are two regions of martensite (and ϵ), these being imaged, from a b.c.c diffraction spot, in Fig. 4.5.4. Thus, it would appear that these two regions

Fig. 4.4

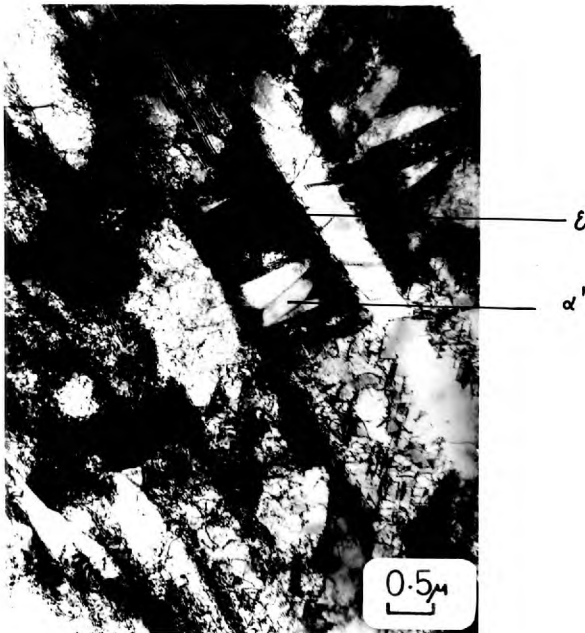


4.4.1. Alloy A. Quenched to -196°C + 2 minutes at 600°C . Cooled in the electron microscope to -60°C .

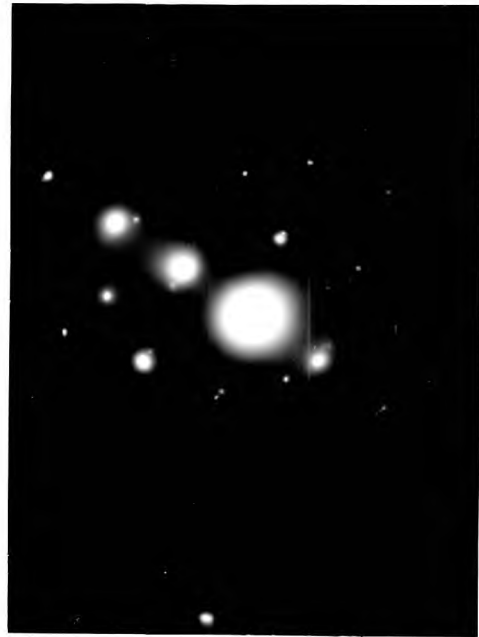


4.4.2. Alloy A. Same area as shown in 4.4.1. Further cooled in the electron microscope to -100°C .

Fig. 4.5



4.5.1. Alloy A. Quenched to -196°C + 2 minutes at 600°C + re-quenched to -196°C .



4.5.2. Alloy A. Selected area diffraction pattern from 4.5.1. showing a (100) b.c.c. pattern + some austenite spots.



4.5.3. Alloy A. Dark field micrograph taken using an f.c.c. reflection in 4.5.2.



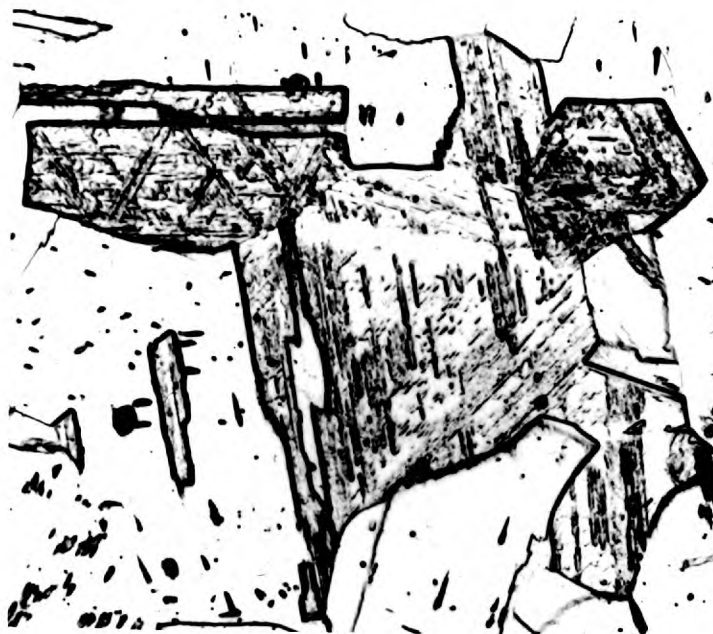
4.5.4. Alloy A. Dark field micrograph taken using a b.c.c. reflection from 4.5.2.

of martensite had formed in a region which had been reversed austenite. It may be noted that the martensitic lath in the centre of Fig. 4.5.1 was much shorter than the normal laths of first generation martensite.

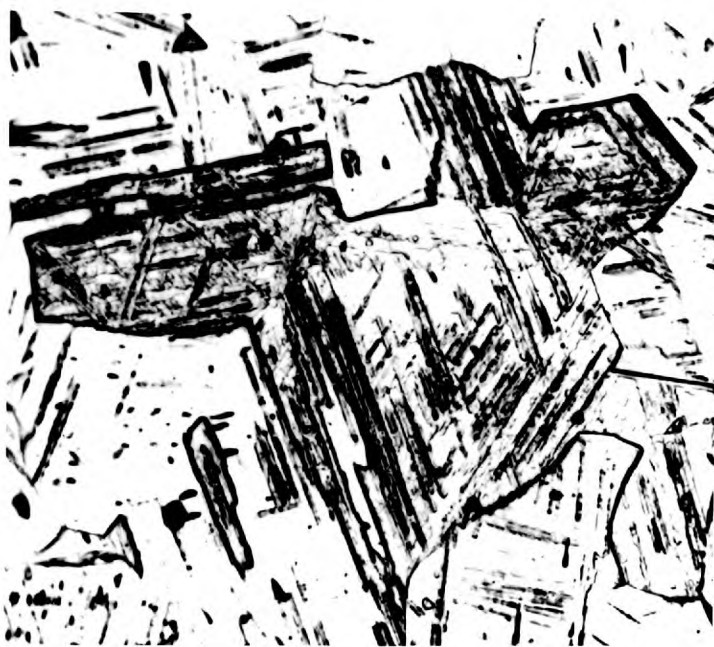
Further evidence of the formation of second generation martensite was obtained by optical microscopy. Fig. 4.6.1 shows lath regions of reversed austenite in a polished and etched specimen. Fig. 4.6.2 shows the same area after simply re-quenching to -196°C and re-photographing. In the regions around the central grain second generation martensite laths can be identified due to the surface tilting produced by the martensite transformation. Comparing the central grain in the two micrographs, no entirely new laths can be detected in Fig. 4.6.2 as compared with Fig. 4.6.1. However, in the area just above the centre of the grain which was not etched fully in Fig. 4.6.1, some tilting can be seen to have occurred which appears to be linked with the laths, present in Fig. 4.6.1, in the adjoining area. Also, several laths in Fig. 4.6.2 appear clearer and less broken than they did in Fig. 4.6.1, possibly indicating that surface tilting had occurred which increased the contrast. Care must obviously be taken in interpreting these micrographs, but the indications are that, at least some second generation martensite formed in the same sites as the first generation martensite, since, (a) no completely new laths were detected in the central grain, and, (b) some of the previous laths were clearer, and possibly extended into under-etched regions in Fig. 4.6.2.

4.1.3 Magnetic Work.

Fig. 4.6



4.6.1. Alloy A. Quenched to -196°C + 2 minutes
at 600°C . x 400



4.6.2. Alloy A. As 4.6.1. + re-quenched to
 -196°C same area as 4.6.1. x 400

Fig. 4.7 shows the effect of reversion temperature (two minute treatments) on the amount of second generation martensite produced by re-quenching to -196°C . 18% martensite was produced by the first quench in liquid nitrogen.

If, after the first quench, the specimens were held for two minutes at $500-530^{\circ}\text{C}$ (below the A_s), and then re-quenched, the amount of martensite could be increased to 24%. However, at temperatures above 530°C when some reversion occurred, the total martensite content after the second quench decreased with increasing reversion temperature until, after complete reversion of the first generation martensite, a second quench produced only 11% martensite. Increasing the reversion temperature to higher temperatures above the A_f then allowed the martensite formed on the second quench to increase.

In order to obtain the amount of martensite formed by the second quench, any remaining first generation martensite must be subtracted from the total martensite content measured after the second quench. The results obtained by this method are shown in the lower graph in Fig. 4.7. It can be seen that the amount of second generation martensite increased with reversion temperature throughout the temperature range.

4.1.4 The Effect of Transformation Cycling on the M_s and A_s

It has been observed^(1,33,48) that transformation cycling causes increasing stabilisation of austenite in both stainless steels and iron-nickel alloys. usually until, after a number of cycles, no martensite can be produced by

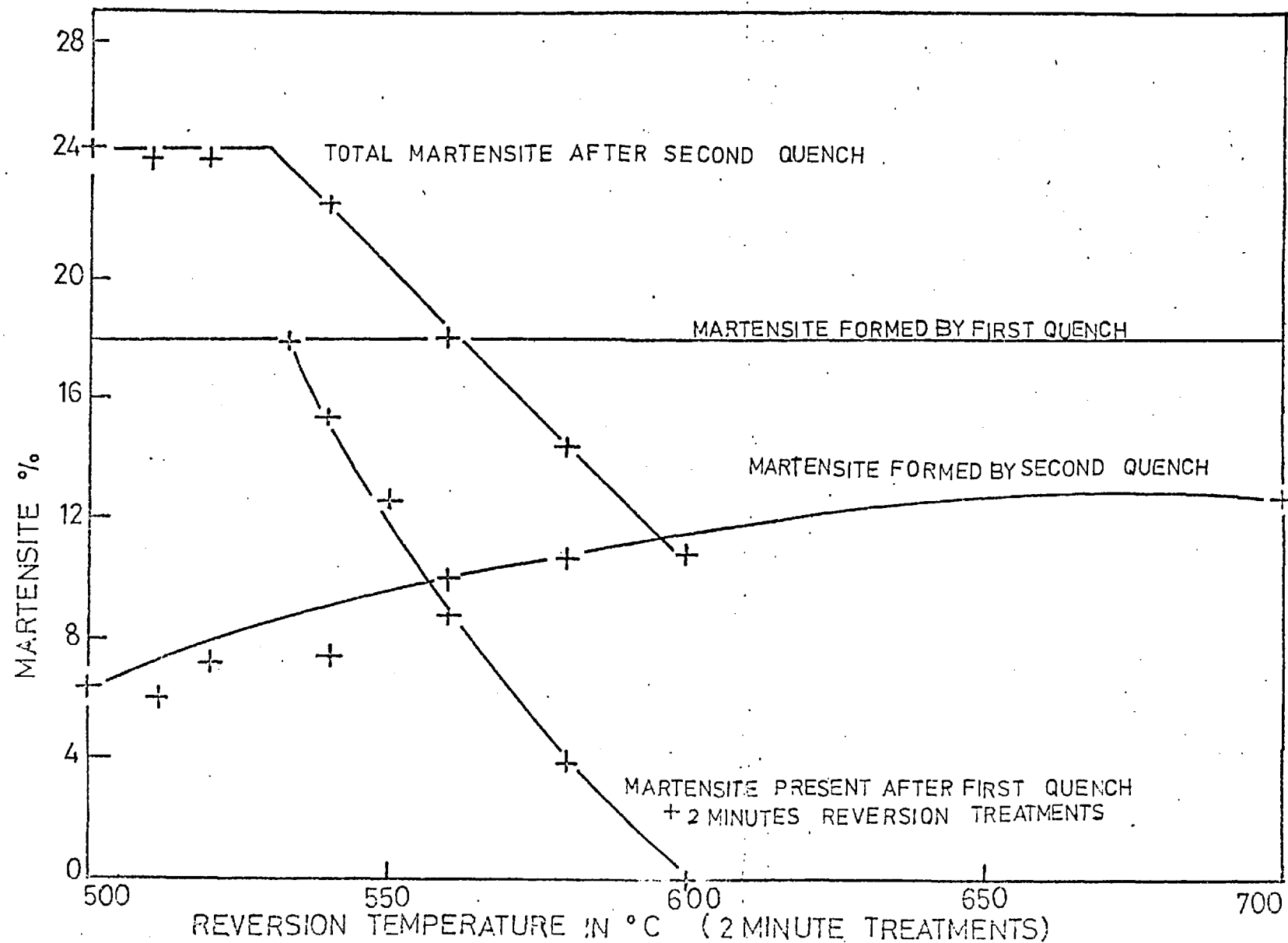


Fig. 4.7. Alloy A. Martensite present after one quench, one quench + one reversion, and a second quench after reversion.

quenching. Therefore, the effect of transformation cycling on the M_s temperature and the reversion temperature range was investigated using a differential dilatometer. The results are shown in Fig. 4.8. The heating rate employed was about $80^\circ\text{C}/\text{minute}$. It can be seen that the M_s decreased slightly with successive cycles of transformation, whilst the A_s and A_f remained unaffected. The small amount of magnetic phase shown after reversion in the fourth and fifth cycles would not revert athermally at temperatures up to 750°C , and was therefore taken to be the stable b.c.c phase observed on isothermal holding as discussed in the previous chapter.

Fig. 4.8 also confirms the observation that less martensite (measured magnetically) is produced by successive quenches after various numbers of reversion treatments. These results are very similar to those obtained by Smith⁽¹⁾.

Fig. 4.8Transformation Cycling in Alloy A.

Cycle	Amount α' %	M_S °C	A_S °C	A_f °C
1st Quench	18.0	-55		
1st Reversion	0		540	600
2nd Quench	12.8	-60		
2nd Reversion	0		540	600
3rd Quench	6.9	-66		
3rd Reversion	0.4		540	600
4th Quench	3.0	-76		
4th Reversion	0.6		540	600
5th Quench	1.6	< -80		
5th Reversion	0.6		540	600

4.2 DISCUSSION

4.2.1 Martensite Formation.

It was mentioned in the review of literature that there has been considerable discussion over the role of ϵ and stacking faults in the martensitic transformation. There are a few observations in the present work which may be discussed in this connection.

Fig. 4.1.1 shows several stacking faults which were not associated with any martensite. This indicates that, at least these stacking faults were not formed as a result of deformation introduced by the martensite transformation. They may have been formed due to a lowering of the stacking fault energy at the beginning of transformation to ϵ . Since very little martensite was observed in the foil it also indicates that stacking faults formed above the M_s . This is in contrast to the results of Goldman et al⁽²⁴⁾ but in support of those of Mangonon and Thomas⁽⁶⁸⁾.

Fig. 4.1.2 shows stacking faults associated with a heavily dislocated region which was probably martensitic. These faults have the appearance of being generated by the martensite rather than of forming before the martensite.

Fig. 4.1.4 shows a dislocated region with a slow-moving boundary. Similar features can be seen in Fig. 4.2 which shows martensite growing sideways from an initial lath by a mixture of bursting and slow growth. It is difficult to say whether the stacking faults in the austenite lying parallel to the martensite boundary in Figs 4.2.1 and 4.2.2 resulted from the martensite transformation or whether they aided in the nucleation of martensite. There is no evidence of the

martensite forming on, or being restricted by, former ϵ laths or plates. The new faults at the top of Fig. 4.2.2 indicate that they were probably generated as a result of the formation of martensite. The faults formed across the boundary in Fig. 4.2.4 seem to be, almost certainly, a result of the impingement of martensite on the other side of the boundary.

Thus, it seems that stacking faults form both before, and as a result of, the formation of martensite. It seems from Fig. 4.2 that ϵ was probably not necessary as an intermediate stage in the transformation to martensite. However, stacking faults were observed in the austenite before martensite formation in thin foils but were not observed after martensite formation in austenite in bulk material, quenched and then examined at room temperature; therefore, they may act as nucleation sites for martensite, possibly transforming to ϵ before doing so.

The part of the transformation involving the slow boundary migration and the formation of heavily dislocated regions of martensite of a different morphology from the normal lath type, was probably associated with transformation in a thin foil. Similar effects have been observed in a stainless steel by Breedis⁽⁸⁾, and in an Fe - 30% Ni alloy by Hull⁽¹⁰⁸⁾ who attributed them to some special effect in thin foils, possibly due to the absence of constraints present in bulk material.

The apparent lowering of the M_s in thin foils as a result of transformation cycling has also been observed in iron-nickel alloys.⁽⁸³⁾ However, there are also examples⁽¹⁰⁸⁾

of thinning raising the M_s in iron-nickel alloys.

Warlimont⁽¹⁰⁹⁾ has attempted to rationalise this situation in a recent article. He suggests that there are two competing mechanisms involved. Firstly, the M_s is raised by "image" forces in a thin foil causing the expansion of nuclei, and, secondly, the M_s is lowered due to the volume of the foil being less than the volume of material required to find a nucleus of high effectiveness. This latter suggestion follows that of Cech and Turnbull⁽¹¹⁰⁾ who found the M_s of a small particle to be lower than that of bulk material.

4.2.2 Second Generation Martensite.

It has been found that the presence of reversed austenite causes stabilisation of austenite both in stainless steels,^(1,48,58) and iron-nickel alloys^(33,35,43,83,84). There have been two main suggestions put forward as to the reason for this stabilisation. Most workers have concluded that the defect structure introduced by the reversed austenite hindered the growth of martensite nuclei. Some workers propounding this defect theory have suggested that a cell network is necessary to hinder the growth of the martensite^(35,63), whilst others^(48,85) have simply attributed it to the high density of tangled dislocations. The other theory for the austenite stabilisation, advanced by Krauss and Cohen⁽⁴⁶⁾, suggests that the diffusion of iron^{and}/or nickel at the martensite/austenite interface prior to reversion causes a change in composition of the austenite and thus its stabilisation. It must be noted, however, that these diffusional effects were observed at very slow heating rates.

Both of these theories involve at least partial prohibition of martensite forming in the same sites in the second generation as it did in the first, since, in stainless steels at least, there is no appreciable deformation of the austenite outside the transformation bands. In the alloys used in the present work, since only 18% martensite was produced by the first quench, it is possible that complete stabilisation occurred in the reversed austenite regions and that second generation martensite formed in regions of retained austenite.

If the second and subsequent generations of martensite formed in the same sites as the first generation, then the continuing stabilisation would presumably have been due to a continuous build-up of the defect structure, or increased diffusion, with each cycle. However, if later generations of martensite formed in regions of retained austenite, then the stabilisation was presumably due to a decrease in the number of nucleation sites with each successive cycle, and possibly, some restrictions on growth of laths by the network of reversed austenite laths.

No conclusive evidence of the sites of formation of second generation martensite was obtained. However, Fig. 4.5 shows that martensite could form in reversed austenite regions, although it may have formed in short lengths i.e. its growth may have been restricted. It is noticeable that ϵ appeared to form with the martensite.

Fig. 4.6 also allows the possibility that second generation martensite may have formed within the same regions as the first generation. Although these micrographs are

difficult to interpret, the general absence of completely new laths, and the darkening and extension of some previous laths as mentioned in the results section, suggests the possibility of successive generations of martensite forming in the same regions.

The literature contains conflicting reports on the sites of formation of second generation martensite. Caron and Krauss⁽⁸³⁾ found successive generations of martensite in an Fe - 30% Ni alloy to form in the same sites, with second generation martensite plates being smaller and narrower than the first generation plates. This correlates well with the current work.

Edmondson and Ko⁽³³⁾, however, found optically, the opposite effect in an Fe - 34% Ni alloy, i.e. that second generation martensite formed in different sites from the first generation martensite. Edmondson & Ko suggested that deformation of the lattice caused by the direct and reverse martensite transformations destroyed the nucleation sites for martensite. Caron and Krauss, however, concluded that the defect structure produced more nucleation sites.

In the present work it seems that second generation martensite probably formed within the same regions as the first generation although Fig. 4.4 indicates that this may not be entirely true since it shows a martensite lath growing into retained austenite. Fig. 4.4 may show an effect unique to transformation in thin foils, or possibly martensite may nucleate at prior martensite boundaries.

Assuming that most of the martensite formed in previously reversed austenite regions, it remains to decide what feature of reversed austenite caused the austenite

stabilisation.

If the stabilisation were caused by the heavy defect structure in the laths inhibiting the growth of martensite, then, as recovery processes proceeded, it would be expected that the stabilisation would gradually decrease. Since recovery occurs faster at higher temperatures the amount of second generation martensite would, therefore, be expected to increase with increasing temperature for the two minute 'reversion' treatments. However, diffusion also occurs faster at high temperatures; thus, if stabilisation were caused by diffusional processes, the amount of second generation martensite would be expected to decrease with increasing 'reversion' temperature. In the diffusional case very little difference would be expected between 600°C and 700°C reversion treatments since complete athermal reversion occurred at both temperatures and no diffusion would be expected after complete reversion. In the case of mechanical stabilisation, however, faster recovery at 700°C would be expected to result in more second generation martensite than would recovery at 600°C.

Fig. 4.7 indicates that the amount of second generation martensite increased with 'reversion' temperature throughout the temperature range from below the A_s to the A_f and also that more second generation martensite was formed after reversion at 700°C than at 600°C. These observations suggest that the stabilisation was a result of the defect structure of the reversed austenite and not diffusional processes. The possibility of diffusional processes is very restricted by the rapid heating and short reversion times, and reference

back to Fig. 3.1 shows that two minutes was too short a time for any diffusion to show up magnetically by the formation of a stable magnetic phase although some diffusion may still have occurred.

These conclusions agree with those of Breedis⁽⁵⁹⁾ who also found that heat treatment just below the A_s enabled more martensite to form on the second quench. He attributed this effect to the decrease in the number of dislocations, stacking faults and twins between the martensite crystals in a lath due to recovery. This suggestion appears valid since second generation martensite formed after 'reversion' treatments below the A_s could not form in the sites of first generation martensite since this was still present. Furthermore, in the present work, no second generation martensite was formed on re-quenching after holding first generation martensite at room temperature. Therefore recovery would appear to have been necessary for the second generation martensite to be produced. Since the dislocation density in the retained austenite was very low, recovery would have very little effect on it. Therefore, it seems that recovery in areas between the martensite crystals, which were previously ϵ , twins or stacking faults, controlled the formation of the second generation martensite. Assuming that each successive generation of martensite formed in these areas between the martensite crystals, even after reversion at 600°C, then the total amount of martensite produced up to complete stabilisation i.e. in five cycles should have been approximately equal to the initial volume of martensite + ϵ + stacking faults present after the first quench. Thus, taking the values in Fig. 8:

The total amount of martensite produced in five cycles

$$= 18 + 12.8 + 6.5 + 2.4 + 1.0.$$

$$= 40.7\%.$$

The volume occupied by laths of martensite + ϵ + stacking faults after the first quench, measured by point counting using an optical microscope, was found to be approximately 45%. These two figures are quite similar and, therefore, allow the possibility that most of the second and subsequent generations of martensite formed in previously ϵ areas of the first quench. This would mean that all the nucleation sites in the austenite which could produce martensite at -196°C were used up in the first quench.

Breedis and Robertson⁽¹⁷⁾ using optical microscopy found a similar result in that, after annealing the reversed austenite in a stainless steel for 15 minutes at 900°C , subsequent quenching to -196°C resulted in martensite forming in the same sites as on the first quench. Thus they concluded that, the same nucleation sites were active but no new ones were produced by this annealing treatment.

Fig. 4.8 indicates that the M_s was depressed by continuous cycling between martensite and austenite. In a similar way, Sastri and West⁽⁸⁴⁾ found the M_s of some medium alloy steels to decrease with increasing austenite yield strength. They suggested that a high austenite dislocation density was associated with a low M_s and a high initial rate of martensite formation. This was because a large number of martensite embryos were present, but their growth was inhibited by an increase in the strain energy associated with the transformation. Breinan and Ansell⁽⁶⁹⁾ found the M_s to

decrease linearly with increasing austenite yield strength in iron-nickel alloys. Since the reversed austenite in the present material had a high dislocation density, and a yield strength above that of annealed austenite, it is probable that the effect on the M_S was caused by factors similar to those proposed by Sastri and West.

In conclusion, it appears that second generation martensite probably forms within the same regions as the first generation laths, possibly in the area which were previously ϵ , stacking faults and twins. The lowering of the M_S and stabilisation of the austenite was probably due to the defect structure of the reversed austenite inhibiting the growth of martensite laths.

The fact that the A_S and A_F were unaffected by transformation cycling, as shown in Fig. 4.8, may indicate that successive generations of martensite were similar in structure to the first generation. This may mean that the martensitic transformation 'swept out' the dislocation structure previously present. This suggestion has also been made by Harvey⁽⁸¹⁾ for martensite forming in deformed ausforming steels.

CHAPTER 5

STRENGTHENING MECHANISMS.

The presence of either martensite or reversed austenite has been observed to increase the strength of an annealed, austenitic, stainless steel. There are a number of possible mechanisms by which this strengthening may occur, viz:

- 1) The increased dislocation density and small grain size will themselves cause an increase in strength;
- 2) The martensite or reversed austenite crystals may act as hard particles, resulting in Orowan strengthening; and
- 3) The laths of martensite or reversed austenite may act as strong fibres in the weaker, annealed austenite matrix, resulting in composite strengthening.

In order to investigate these mechanisms, experiments were performed on alloy A to determine the dependence of the strength on the amount of martensite or reversed austenite present. Also some observations were made in the electron microscope of structures, containing reversed austenite which had been deformed a small amount.

5.1 RESULTS

Fig's 5.1 to 5.3 show the variation in hardness, tensile strength and ductility with increasing amounts of martensite and reversed austenite. The martensite was induced by quenching for 15 minutes or longer at -70°C , -100°C , and -196°C . The largest amount of martensite (23.5%) was produced by quenching to -196°C , followed by an intermediate anneal of 2 minutes at 500°C and re-quenching; therefore the results from these specimens may be unreliable, although they appear to fit reasonably on the graphs. The reversed austenite was produced by 2 minute heat treatments at 600°C .

Fig. 5.1 shows the variation in hardness with the amounts of martensite and reversed austenite. In neither case was the graph linear, the slope decreasing with increasing martensite or reversed austenite content. At each level of second phase the partially martensitic specimens were harder than the austenitic.

Fig. 5.2 shows various tensile properties at 150°C (above the M_d) of partially martensitic specimens, plotted against the martensite content. The 0.2% proof stress and the U.T.S. appear to have increased linearly with increasing martensite content, the slope of the proof stress graph being slightly greater than that of the U.T.S. The ductility decreased rapidly with increasing martensite content, although the largest decrease appears to have occurred over the first few per cent of martensite. The work hardening rate was found to increase with increasing martensite content.

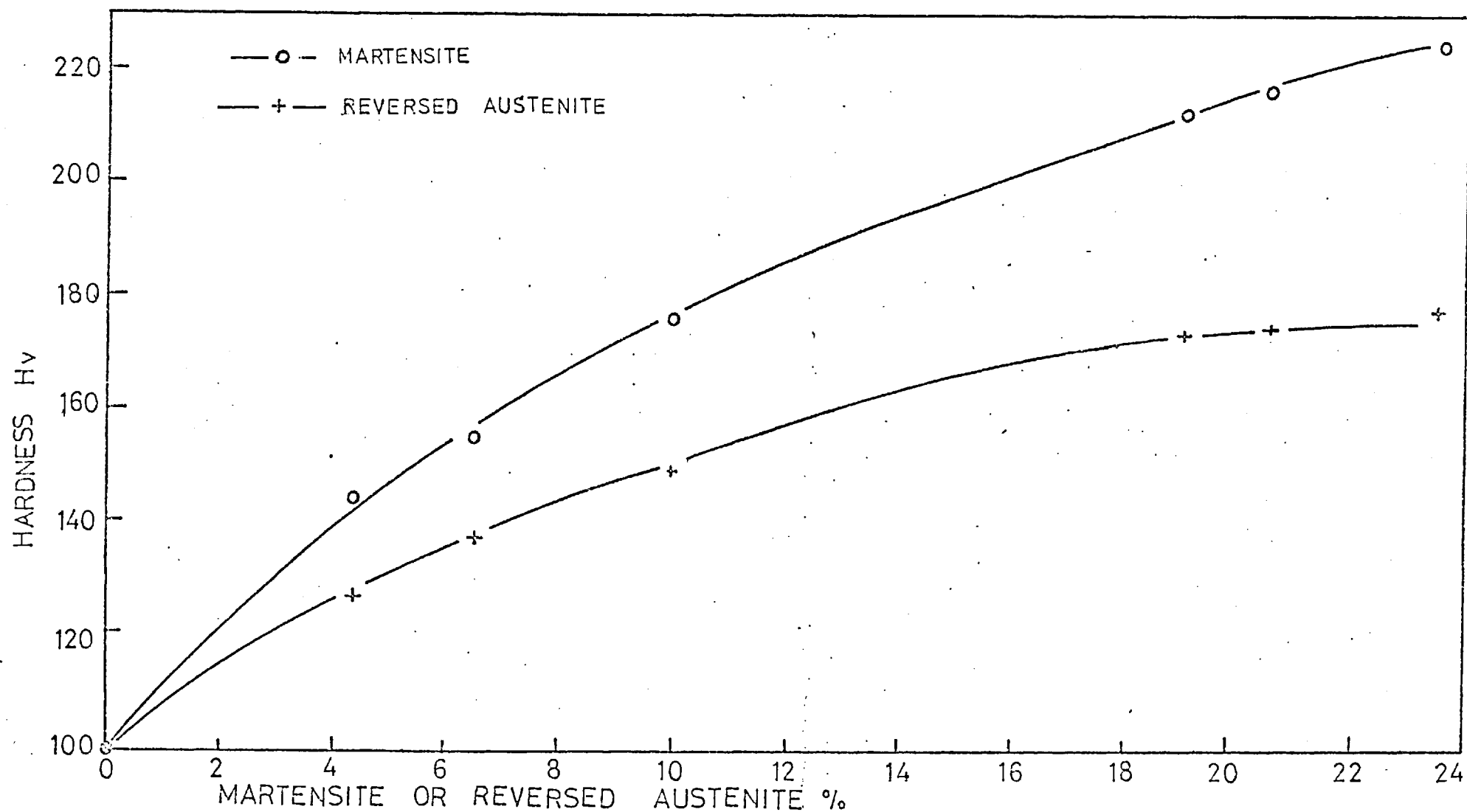


Fig. 5.1. Alloy A. Hardness changes with increasing amounts of martensite or reversed austenite.

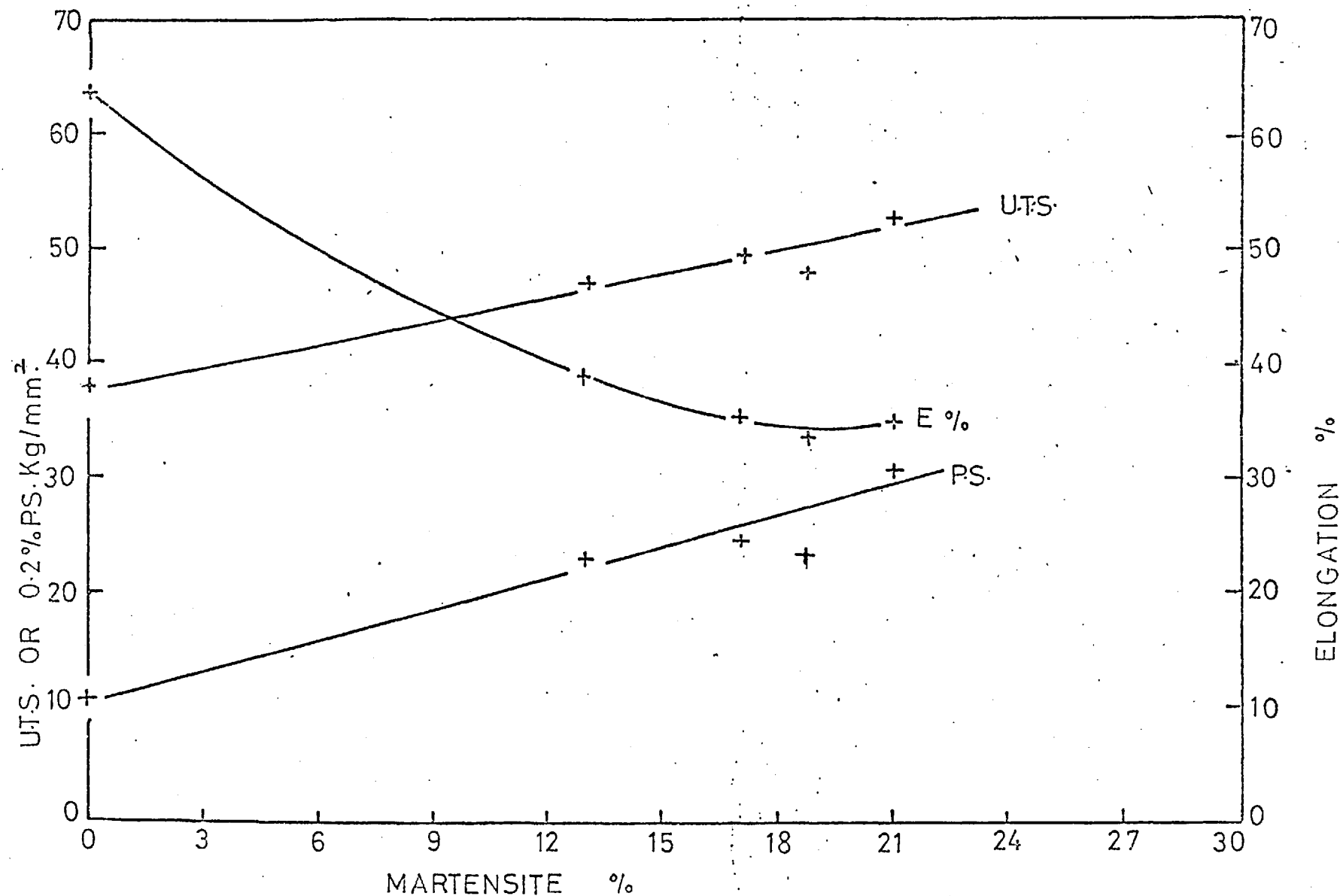


Fig. 5.2. Alloy A. Changes in proof stress, U.T.S. and ductility with increasing martensite content.

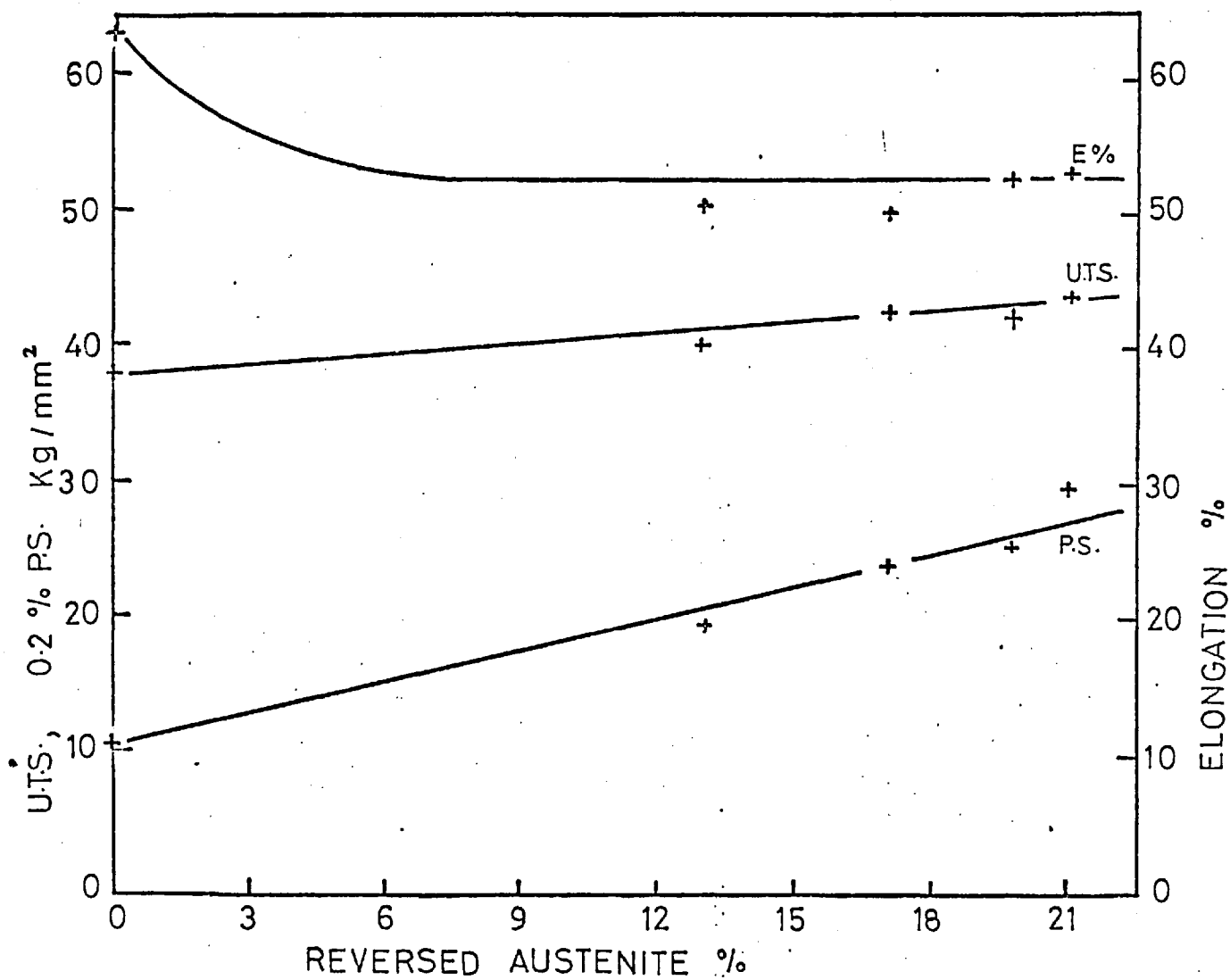


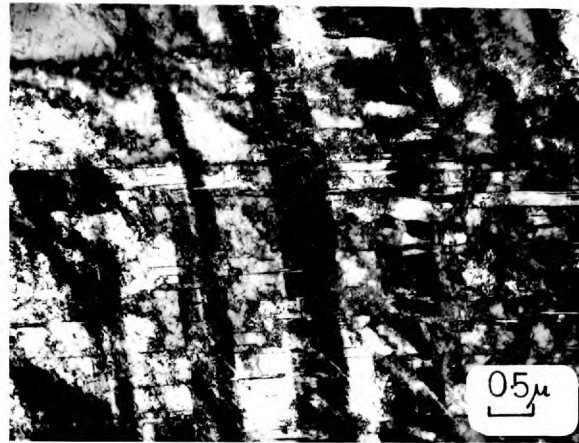
Fig. 5.3. Alloy A. Changes in proof stress, U.T.S and ductility with increasing reversed austenite content.

Fig. 5.3 shows the same properties as Fig. 5.2, this time for specimens containing reversed austenite rather than martensite. The 0.2% proof stress and the U.T.S again increased linearly with increasing reversed austenite, but the slope of the U.T.S. graph was considerably lower than that of the proof stress graph. The U.T.S., in fact, was not increased very markedly by the presence of reversed austenite, whilst the proof stress increased at almost the same rate as with increasing martensite content. The ductility remained relatively high at all levels of reversed austenite, the major decrease in ductility occurring over the first few percent of reversed austenite, after which it remained fairly constant. The work hardening rate was found to decrease with increasing reversed austenite content.

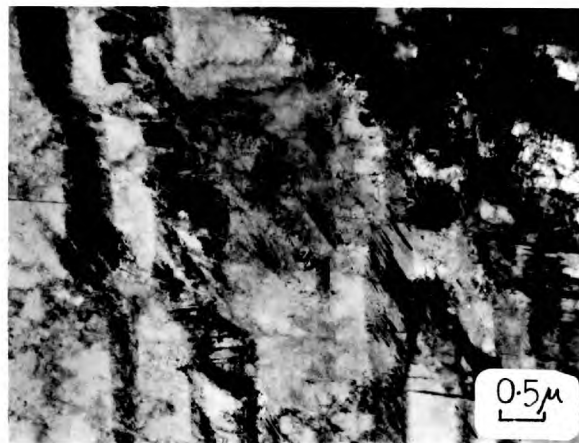
In an attempt to gain information about the manner in which reversed austenite laths behaved under deformation, some material was quenched, reversed, deformed approximately 5% by rolling, and then examined in an electron microscope. Some of the structures observed are shown in Fig. 5.4. Fig. 5.4.1 shows several laths of reversed austenite running down the micrograph which appear to have been cut by needle-shaped features running across the micrograph. These needle-like features resemble very narrow laths of deformation-induced martensite such as were observed in the present work on deformation-induced martensite (see Fig. 6.2.1). The right hand reversed austenite lath in Fig. 5.4.1 particularly appears bent by the deformation. The boundaries of the laths appear fairly diffuse and merge into the deformed

austenite around them, often without a clearly defined boundary. Fig. 5.4.2 shows two laths, at the top of the micrograph, which appear to have been sheared in places by the deformation. Fig. 5.4.3 shows an area which has the appearance of having been a reversed austenite lath (running diagonally across the micrograph from the top left hand corner to the bottom right hand corner); this region now seems generally deformed and to be losing its identity as a distinct lath.

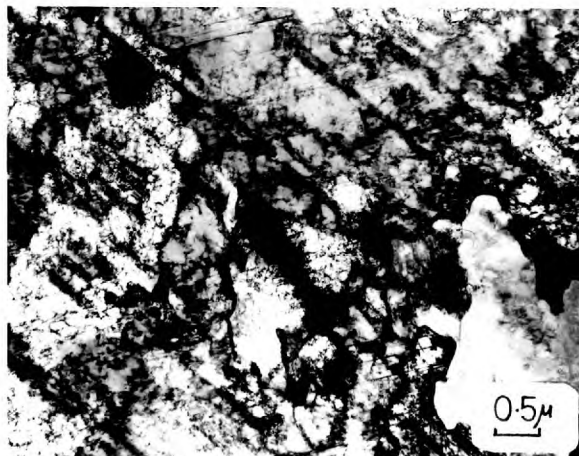
Fig. 5.4



5.4.1. Alloy A. Quenched to -196°C + 2 minutes at 600°C + 5% deformation by rolling at room temperature.



5.4.2. Alloy A. As 5.4.1.



5.4.3. Alloy A. As 5.4.1.

5.2 DISCUSSION

The factors which may contribute to the strength of metals are generally accepted as being:

- 1) Friction Stress.
- 2) Grain Size.
- 3) Solid Solution Strengthening.
- 4) Precipitation or dispersion strengthening.
- 5) Substructure (dislocations, twins etc.)
- 6) Number, Structure and Morphology of Phases present.
- 7) Ordering.

In explaining the increased strength of reversed austenite as compared with annealed austenite, the friction stress and solid solution strengthening can be considered the same for both structures since their composition and atomic structure are the same. In alloy A precipitation can also be discounted since the very low carbon content and the short times spent at high temperatures make any precipitation very unlikely. No ordering would be expected in these alloys. Thus, the possible strengthening mechanisms are the grain size effect, the substructure, and the possible dispersion or composite hardening effect of relatively strong laths of reversed austenite in a weak matrix of retained austenite.

Fig. 5.3 indicates that the presence of reversed austenite in a solution treated austenite structure increased the 0.2% proof stress, had only a small effect in increasing the U.T.S., and reduced the ductility and work hardening

capacity. These results are similar to those obtained with iron-nickel alloys by a number of other workers^(34, 46, 48, 75, 77). The general conclusion of the workers on iron-nickel alloys was that the strength increase was mainly due to an increased dislocation density, although the strengthening effect of the increased crystal misorientation was also emphasised by Krauss and Cohen⁽⁴⁶⁾. Gorbach and Malyshev⁽⁷⁷⁾ were able to obtain up to 80% martensite by quenching, in an Fe - 30% Ni alloy, and so produced a graph of the dependence of yield stress on reversed austenite content over a wider range of reversed austenite contents than was possible in the present work. They found that the yield stress rose sharply for the first 20% of reversed austenite, then increased to a much smaller extent with the next 40% reversed austenite, finally rising sharply again from 70 to 80% reversed austenite. They state that this behaviour is similar to that produced by increasing plastic deformation (at least up to 70% reversed austenite).

In the present work, the very small increase in U.T.S but larger increase in proof stress, together with the decreased work hardening rate with increasing reversed austenite, suggest that the main strengthening mechanism may have been the increased dislocation density as in iron-nickel alloys. If dispersion or composite hardening were involved to any large extent the work hardening rate and U.T.S would be expected to increase as well as the proof stress.

Conrad^(111,117) suggested a general equation for

the flow stress produced by various mechanisms such that:

$$\sigma_f = \sigma_i + \alpha_1 \mu b \rho^{\frac{1}{2}} + \alpha_2 \mu b \lambda^{-1} + K d^{-\frac{1}{2}} \quad (1)$$

where σ_f = The flow stress.

σ_i = The thermal component of the stress

α_1 and α_2 are numerical factors.

μ = The shear modulus of iron.

b = The Burger's vector.

ρ = The Dislocation density.

λ = The inter-particle spacing of precipitates.

d = The grain size.

and K is a function of the stress necessary to activate a dislocation source.

Since there were no precipitates present in alloy A, the term involving λ may be neglected. The overall grain size of the solution treated austenite was retained throughout the quenching and reversion process. Although a large number of fine grains were present in the reversed austenite, their boundaries would have been generally low angle⁽¹⁾, and therefore it seems probable that the grain size contribution to the increased strength of reversed austenite would have been quite small. Thus, since all measurements were performed at the same temperature so allowing σ_i to be neglected, the increase in proof stress produced by reversed austenite,

$$\sigma_f' = \alpha \mu b (\rho_1^{\frac{1}{2}} - \rho_2^{\frac{1}{2}}) \quad (2)$$

where ρ_1 = The Dislocation density of the structure containing reversed austenite.

and ρ_2 = The Dislocation density of solution treated austenite.

$$\alpha = 0.4$$

$$\mu = 8.5 \times 10^3 \text{ kg/mm}^2$$

$$b = 2.5 \times 10^{-8} \text{ cm.}$$

Thus, taking the proof stress values from Fig. 5.3 at 20% and 0% reversed austenite, and putting them into equation (2) together with the assumption that the dislocation density of solution treated austenite was 10^8 lines/cm^2 , it is found that the overall dislocation density at 20% reversed austenite would correspond to approximately $6 \times 10^{10} \text{ lines/cm}^2$. If a mixture rule is assumed such that the overall dislocation

$$\rho_A = f_{R.A.}(\rho_{R.A.}) + (1 - f_{R.A.})(\rho_{S.T.A.})$$

where $f_{R.A.}$ = The volume fraction of reversed austenite present

$\rho_{R.A.}$ = The dislocation density in reversed austenite

and $\rho_{S.T.A.}$ = The dislocation density in solution treated austenite.

It is found that the dislocation density in the reversed austenite would be approximately $3 \times 10^{11} \text{ lines/cm}^2$.

Whilst it was found to be impossible to measure the dislocation density in the reversed austenite, this figure seems reasonable.

If this dislocation density mechanism were operative the relationship between the proof stress and percentage reversed would not be expected to be linear but parabolic, since $\sigma \propto \rho^{\frac{1}{2}}$. However, an examination of the graphs of Gorbach and Malyshev reveals that the yield stress increased almost linearly with increasing reversed austenite for the first 20% but then decreased rapidly from the linear relationship up to 70%. This high initial rate

of increase in strength may be explained in terms of the morphology of the reversed austenite. Since the increased dislocation density associated with the presence of reversed austenite was contained in distinct laths, the basic structure at very low levels of reversed austenite was still that of annealed austenite. Therefore, at the same average overall dislocation density, a partially reversed austenite structure would not result in as large an increase in strength as if the dislocation density had been uniform over the specimen, since more dislocation inter-actions would then have occurred. As the amount of reversed austenite increased, however, the higher dislocation density occurred over a larger volume of the specimen, and so the effect of restricting the high dislocation density to distinct laths decreased. Thus, although an average increase in dislocation density would have resulted in a parabolic increase in strength, the morphology of the reversed austenite modified this to a linear relationship at low levels of reversed austenite.

Fig. 5.5 shows the strain at which deformation of annealed austenite at 150°C produced an equivalent flow stress to the yield stress at 150°C of structures containing various amounts of reversed austenite. This shows that the first 12% of reversed austenite was equivalent to only 4% deformation, but with increasing reversed austenite above this level, the equivalent deformation increased more rapidly. This observation supports the above suggestion that the morphology of the reversed austenite affected the strengthening increment.

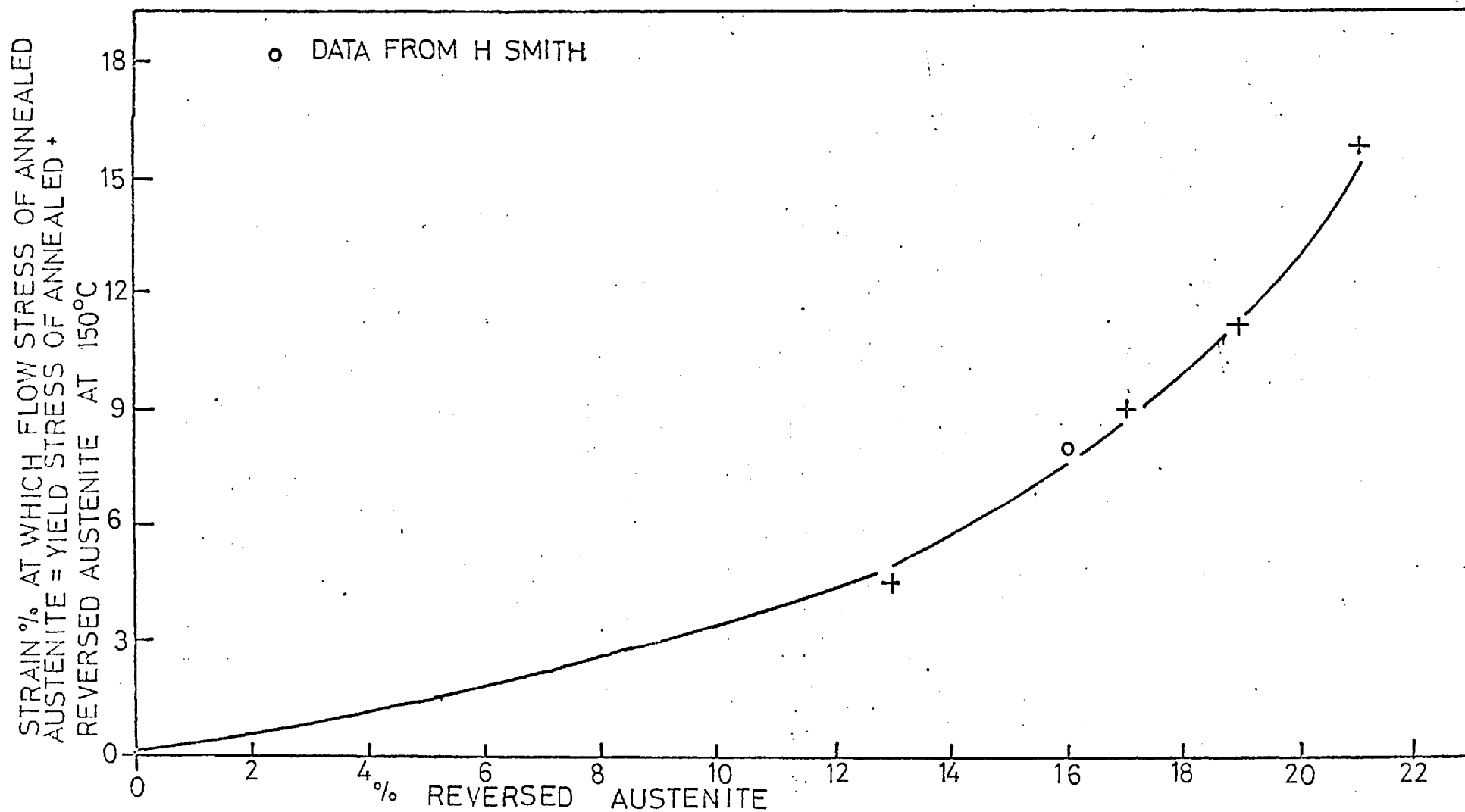


Fig. 5.5. Alloy A. The tensile strain required at 150°C to make the flow stress of annealed austenite equal to the yield stress of material containing various amounts of reversed austenite.

Extrapolating the proof stress line linearly in Fig. 5.3 to 100% reversed austenite, produces a figure for the strength of reversed austenite of 92.5 kg/mm^2 . Putting this figure into equation (2) produces a result for the dislocation density of $10^{12} \text{ lines/cm}^2$. This figure seems rather high and suggests that if the graph continued linearly then some other strengthening mechanism would have to be postulated. However, taking the dislocation density of reversed austenite as 3×10^{11} as calculated above, and using equation (2) which predicts a parabolic form of yield stress vs dislocation density graph, it is found that the strength at 100% reversed austenite would be approximately 55 kg/mm^2 . Unfortunately this could not be checked experimentally, but it is a somewhat larger strengthening increment than has been found in iron-nickel alloys.^(34,46,57,75) This may be due to a larger dislocation density being produced in the lath martensites formed in stainless steels, than in the plate martensites in iron-nickel alloys.

Thus, it seems reasonable to suggest that the basic strengthening mechanism of reversed austenite is the high dislocation density. The micrographs in Fig. 5.4 also support this conclusion by showing that the reversed austenite/laths may be deformed and do not remain complete laths acting as a stronger phase.

The similarity of the increase in proof stress with increasing martensite content shown in Fig. 5.2, to that for reversed austenite shown in Fig. 5.3, may indicate that a similar mechanism was involved in raising the yield stress. However, the increasing U.T.S and work hardening rate with

increasing martensite, indicate that a different mechanism to that in reversed austenite was involved in the work hardening.

Extrapolating the proof stress line in Fig. 5.2 to 100% martensite produces a figure for the 0.2% proof stress of approximately 95 kg/mm^2 . Extrapolating the line in Fig. 6.4 for the 0.2% proof stress of alloy A for structures containing various amounts of deformation-induced martensite and deformed austenite, to 100% deformation-induced martensite, produces a figure for the 0.2% proof stress of approximately 76 kg/mm^2 ; however, it must be emphasised that this graph was produced from compression tests, whereas the quenched structures were tested in tension. These figures seem to indicate that the values of the 0.2% proof stress do not continue to rise linearly with increasing quench-induced martensite.

Mangonon and Thomas⁽⁶⁸⁾, however, found a linear relationship between yield stress and deformation-induced martensite content from 0 - 100% martensite in an 18/8 stainless steel. They suggested two possible explanations of this linear relationship, namely, dispersion strengthening and composite strengthening. They dismissed dispersion strengthening on the grounds that the inter-particle spacing, taking the martensite crystals as hard particles, was too large to explain the strength increase. This conclusion also seems valid in the present case although the characteristic inhomogeneity of the martensite transformation made the inter-particle spacing impossible to measure. Mangonon and Thomas therefore concluded that the strengthening was probably due to a composite mechanism. The same conclusion

is possible in the present work although the laths were not observed to be aligned in one direction. Mangonon and Thomas seem to have neglected the possibility of transformation plasticity affecting their results, or the effect of increasing deformation on the strength of the retained austenite.. These aspects are discussed more fully in the following chapter on deformation-induced martensite but throw some doubt on the suggestions that the yield strength does not continue to rise linearly with martensite content up to 100%.

The suggestion of composite strengthening would explain the increase in work hardening rate with increasing martensite content; however, the difference in the work hardening behaviour of the structures containing martensite compared to those containing reversed austenite may also be explained in terms of the structures of the two phases. In the martensitic specimens, the b.c.c. martensite is inherently stronger than the f.c.c. matrix (austenite), the slip systems are different in the two phases, and the boundaries around the martensite crystals are high angle. In the reversed austenite case, however, both phases are f.c.c. and therefore have the same slip systems, and the boundaries in the reversed austenite are low angle. The barriers to dislocation movement are therefore much greater in the case of the martensite than in that of the reversed austenite.

The non-linearity of the hardness curve shown in Fig. 5.1 for reversed austenite as compared with the proof stress graph in Fig. 5.3 can be explained by the work hardening rate decreasing with increasing reversed austenite content. However, in the case of martensitic specimens the hardness curve in Fig. 5.1 is also non-linear, but the work

hardening rate was observed to increase with increasing martensite content. One possible explanation is the formation of martensite during the hardness tests, more martensite forming when less martensite was originally present.

CHAPTER 6.

DEFORMATION INDUCED MARTENSITE.

Although the formation of martensite in heavily cold worked stainless steels has been investigated by a number of workers^(9,14,15,27,68), there have been very few studies of the reversion of this martensite to austenite. This transformation has, therefore, been investigated using 50% cold rolled material examined magnetically, mechanically and in the electron microscope. Both Alloy A and Alloy B were used in this investigation.

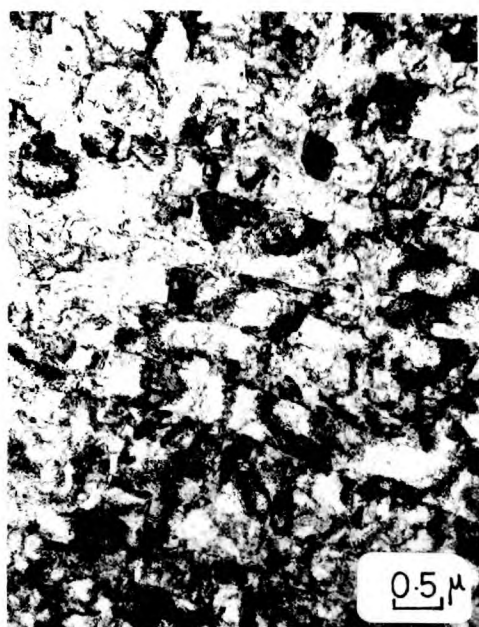
6.1 RESULTS.

6.1.1 The Formation of martensite.

The martensite was produced by standard 50% rolling deformations, the amount of martensite being varied by varying the rolling temperature between $+150^{\circ}\text{C}$ and -78°C . The rolling was carried out in several passes of 10% reduction or less, time being allowed between passes for the specimens to cool to the relevant temperature.

At -78°C 50% deformation of alloy A produced 85% martensite, and of alloy B, 90% martensite. Some of the structures produced at this temperature are shown in Figs. 6.1 - 6.3. Figs. 6.1 and 6.2 show the structures of alloys A and B respectively taken from a section parallel to the rolling plane. The lath-like structure produced was very similar to that found for quench-induced martensite although very little ϵ was visible in contrast to the quenched

Fig. 6.1.



6.1.1. Alloy A. Rolled 50%
at -78°C .



6.1.2. Alloy A. Dark field
micrograph of same area as
6.1.1. taken using a martensite
reflection.

Fig. 6.2.



6.2.1. Alloy B Rolled 50%
at -78°C . 90% martensite
present



6.2.2. Alloy B. As 6.2.1.

structure. The lack of ϵ was probably due to its almost complete transformation to martensite since ϵ has been found^(27,68) to form in these types of steel. The lath structure is most clearly shown in Fig. 6.2.1 for alloy B where three sets of laths at 60° angles to each other can be distinguished. The foil orientation for these micrographs was such that the surface was parallel to $(111)_\gamma$. The dark field micrograph in Fig. 6.1.2 shows clearly that the laths contained small grains of martensite of the order of 0.5μ in diameter. Comparison of Figs. 6.2.1 and 6.2.2 shows clearly the inhomogeneity of the martensitic transformation since these were two areas from the same foil.

In order to establish more clearly the morphology of the martensite, sections were taken in the longitudinal direction normal to the rolling plane, and in the transverse direction. Micrographs illustrating the structures observed are shown in Fig. 6.3 for alloy B. Lath structures can again be seen in Figs. 6.3.2 and 6.3.3 although these appeared somewhat narrower than in the plane parallel to the rolling plane, their width being of the order of 0.1μ . In other areas and orientations the lath structure was not so clearly observed. e.g. Figs. 6.3.1 and 6.3.4 where a more generally deformed structure was observed. The small grains of martensite can again be distinguished in these generally deformed structures in Figs. 6.3.1 and 6.3.4, where they have produced the appearance of a fine cell structure.

6.1.2 Mechanical Properties of the Martensite.

The effect of the presence of martensite on the

Fig. 6.3



6.3.1. Alloy A. Rolled 50%
at -78°C . Longitudinal
section perpendicular to
the rolling plane.



6.3.2. Alloy A.
As 6.3.1.



6.3.3. Alloy A. Rolled 50%
at -78°C . Transverse section.



6.3.4. Alloy A.
As 6.3.3.

mechanical properties of austenite was investigated using hardness measurements and compression tests. Fig. 6.4 shows the variation in hardness and 0.2% proof stress with the amount of martensite produced by 50% deformation at various temperatures of alloy A and alloy B.

For Alloy A the 0.2% proof stress can be seen to have increased linearly with increasing martensite content, but the hardness, although increasing with increasing martensite, did not do so linearly. The work hardening rate observed from the compression tests was also found to increase with increasing martensite content.

For alloy B the graph was more complex. Initially the hardness increased at a greater than linear rate with increasing martensite, but when the rolling temperature fell below 0°C the hardness suddenly dropped even though the martensite content continued to rise. Between the rolling temperatures of -20°C and -78°C the hardness increased very rapidly with a small increase in martensite content.

It must be mentioned that other variables, particularly the deformation temperature, may have affected the strength of the material in addition to the variation in martensite content.

In order to attempt to establish if dynamic strain ageing at 20°C and above was responsible for the sudden drop in hardness between $+20^{\circ}\text{C}$ and 0°C on rolling alloy B, internal friction tests were carried out on specimens rolled at room temperature and -20°C . No free carbon was detected in either case. The reason for this may have been that, with 15% Chromium in the alloy, the carbon was not free but associated

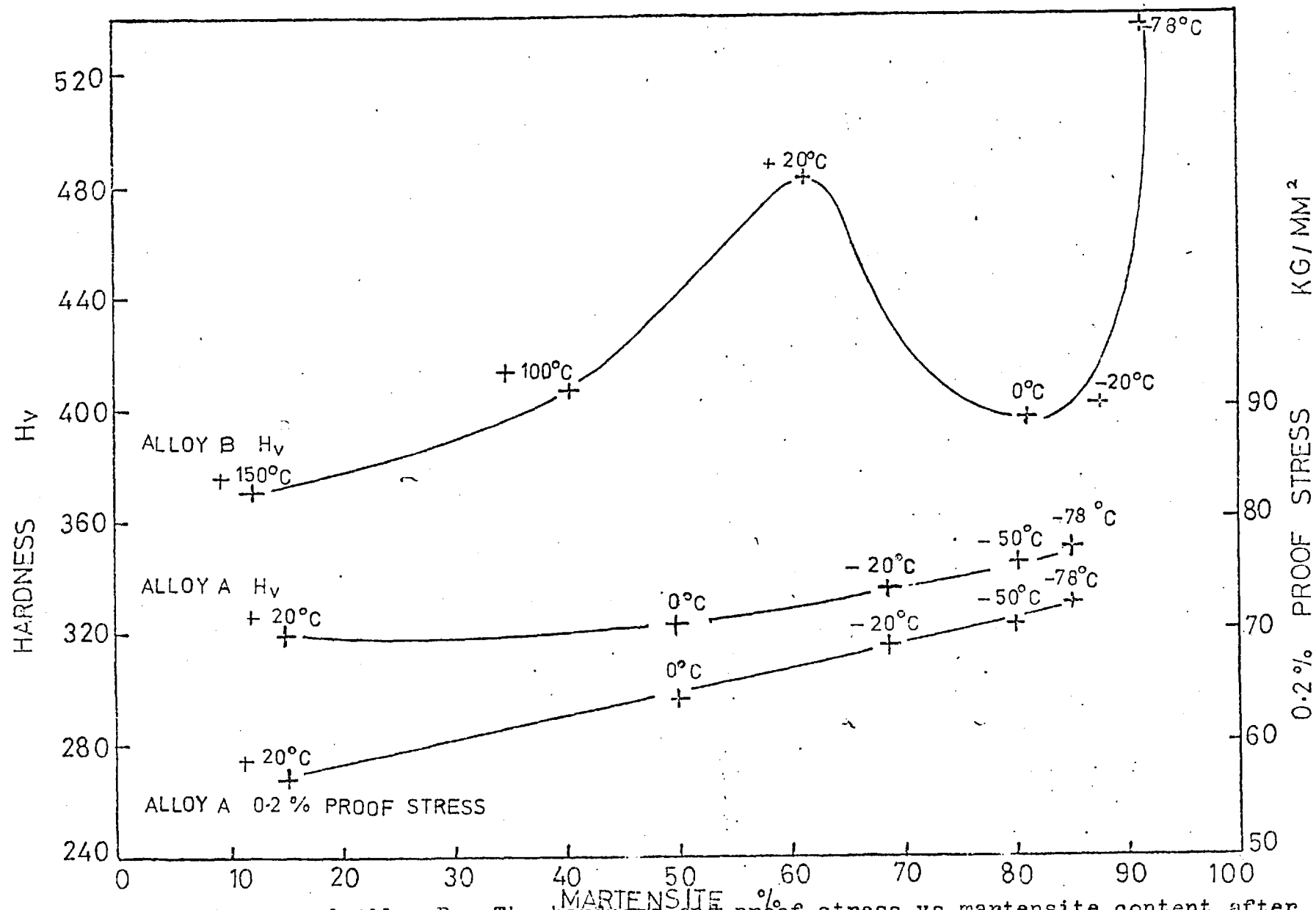


Fig. 6.4. Alloy A and Alloy B. The hardness and proof stress vs martensite content after 50% deformation at various temperatures.

with chromium atoms. Also static strain ageing may have occurred on holding at room temperature.

6.1.3 Transformation Plasticity.

Plastic deformation and transformation to martensite have been described⁽¹¹²⁾ as competing modes of deformation in alloy steels. In order to investigate the effect of martensite formation on the deformation characteristics of alloys A and B tensile tests were performed at various temperatures in baths of acetone or silicone oil. The proof stress, tensile strength and percentage elongation values obtained are shown in Figs. 6.5 and 6.6. Due to lack of material, only one specimen was tested in each case. In all tests where martensite was formed the stress-strain curves were serrated; also occasional large drops in stress indicated bursts of transformation. In alloy A a peak in ductility was observed in Fig. 6.5 for deformation at 0°C. In alloy B, Fig. 6.6 indicates a much larger ductility peak at the higher temperature of about +80°C. The U.T.S. rose in both alloys with decreasing test temperatures, whilst the proof stress values were essentially unchanged.

6.1.4 Mechanical Properties of Structures containing Reversed Austenite.

In order to investigate the properties of reversed, deformation-induced martensite, specimens were taken after the rolling treatments described in section 6.1.2, reversed in a salt bath at various temperatures for two minutes, and then tested using hardness measurements and compression tests.

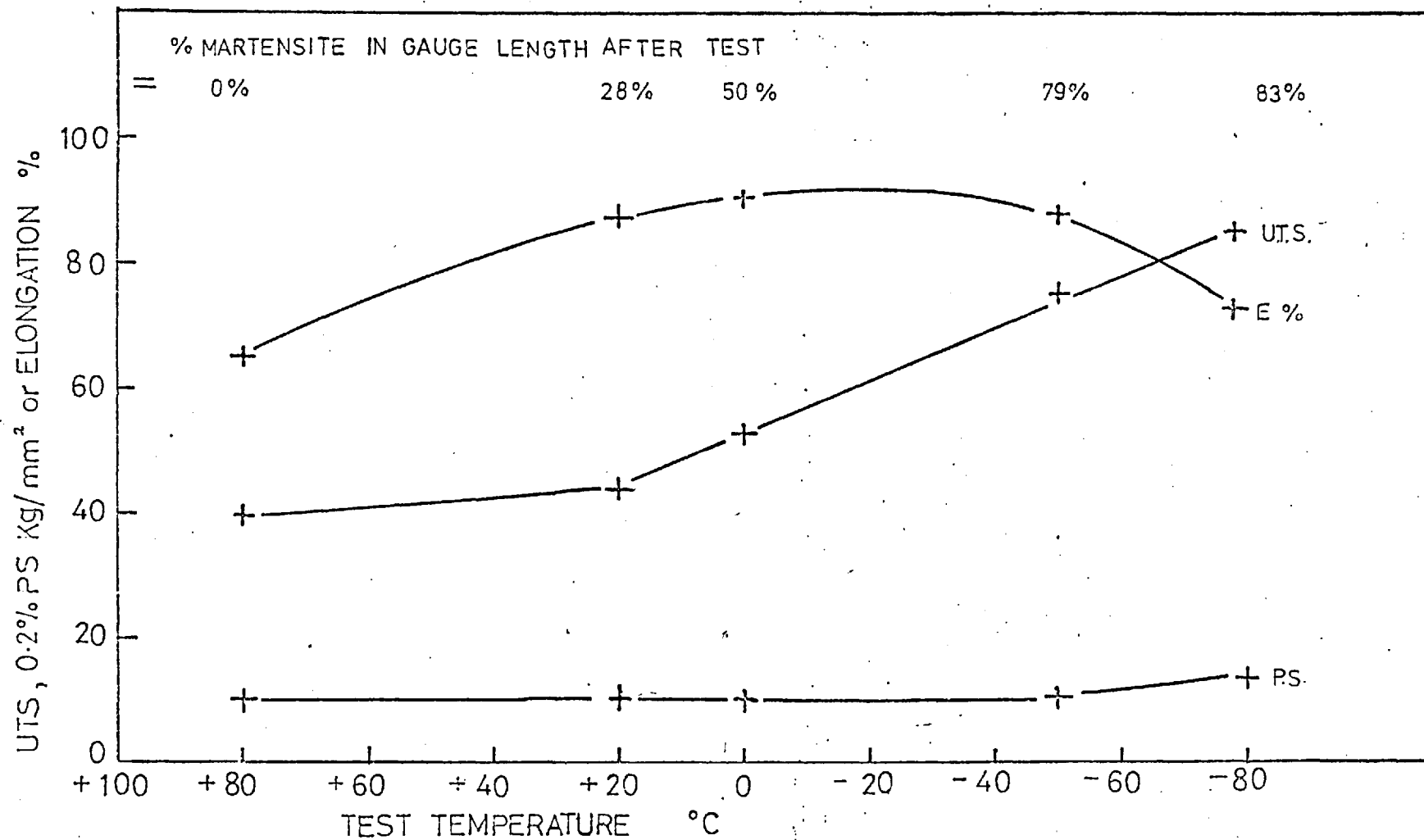


Fig. 6.5. Alloy A. Proof stress, U.T.S. and ductility values from tensile tests performed at various temperatures.

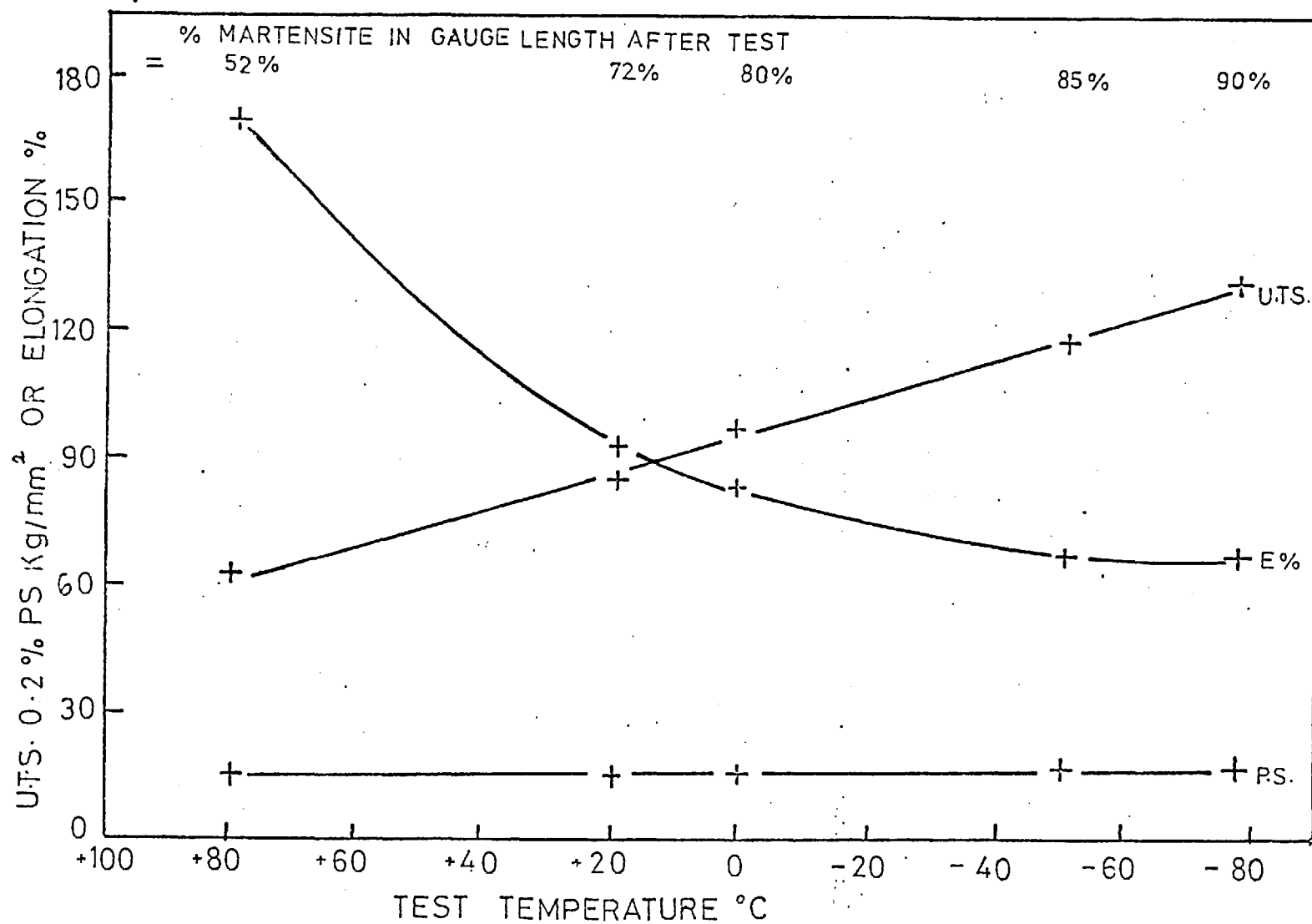


Fig. 6.6. Alloy B. Proof stress, U.T.S and ductility values from tensile tests performed at various temperatures.

The results, presented in Figs. 6.7 and 6.8 for alloy A and Fig. 6.9 for alloy B, show the hardness and 0.2% proof stress of the specimens as a function of the martensite content after rolling.

In alloy A the specimens were found to be fully reversed after two minutes at 600°C . In this alloy, for reversion treatments at 600°C and 650°C the hardness and proof stress increased slightly with increasing original martensite content up to 50% martensite, and then decreased markedly on increasing the martensite to between 50 and 85%. Reversion of the specimens deformed at room temperature (containing 15% martensite) at 600°C and 650°C resulted in ~~very~~ little change in the hardness or proof stress from their values after rolling. However, reversion at 700°C and above resulted in a large fall in the hardness and proof stress values for all rolling temperatures. After reversion at 700°C and above, the hardness and proof stress remained virtually unchanged from 15 to 50% original martensite, but then increased with increasing original martensite from 50 to 85%. For all rolling temperatures the hardness and proof stress decreased with increasing reversion temperature, with a sharp decrease occurring between 650° and 700°C . This sharp decrease was less pronounced at higher levels of martensite.

The results obtained for alloy B, shown in Fig. 6.9, were somewhat more complex than those for alloy A. Since the reversion temperatures for alloy B were higher than those for alloy A the specimens reversed at temperatures between 650°C and 750°C contained some retained martensite; however, this does not seem to have made the shape of the curves any

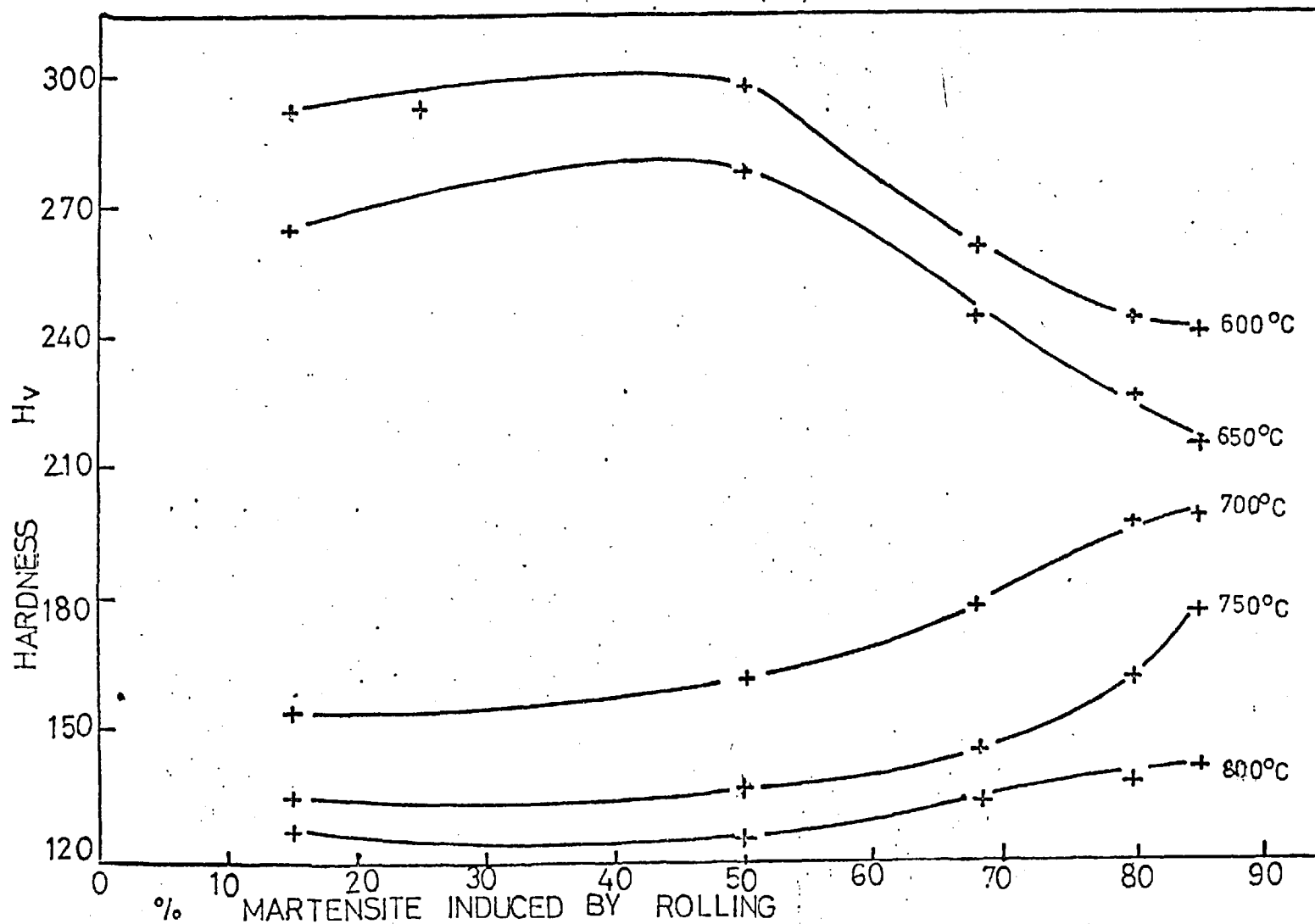


Fig. 6.7. Alloy A. Hardness vs reversed austenite content for material deformed 50% at various temperatures and then heated for two minutes at various reversion temperatures.

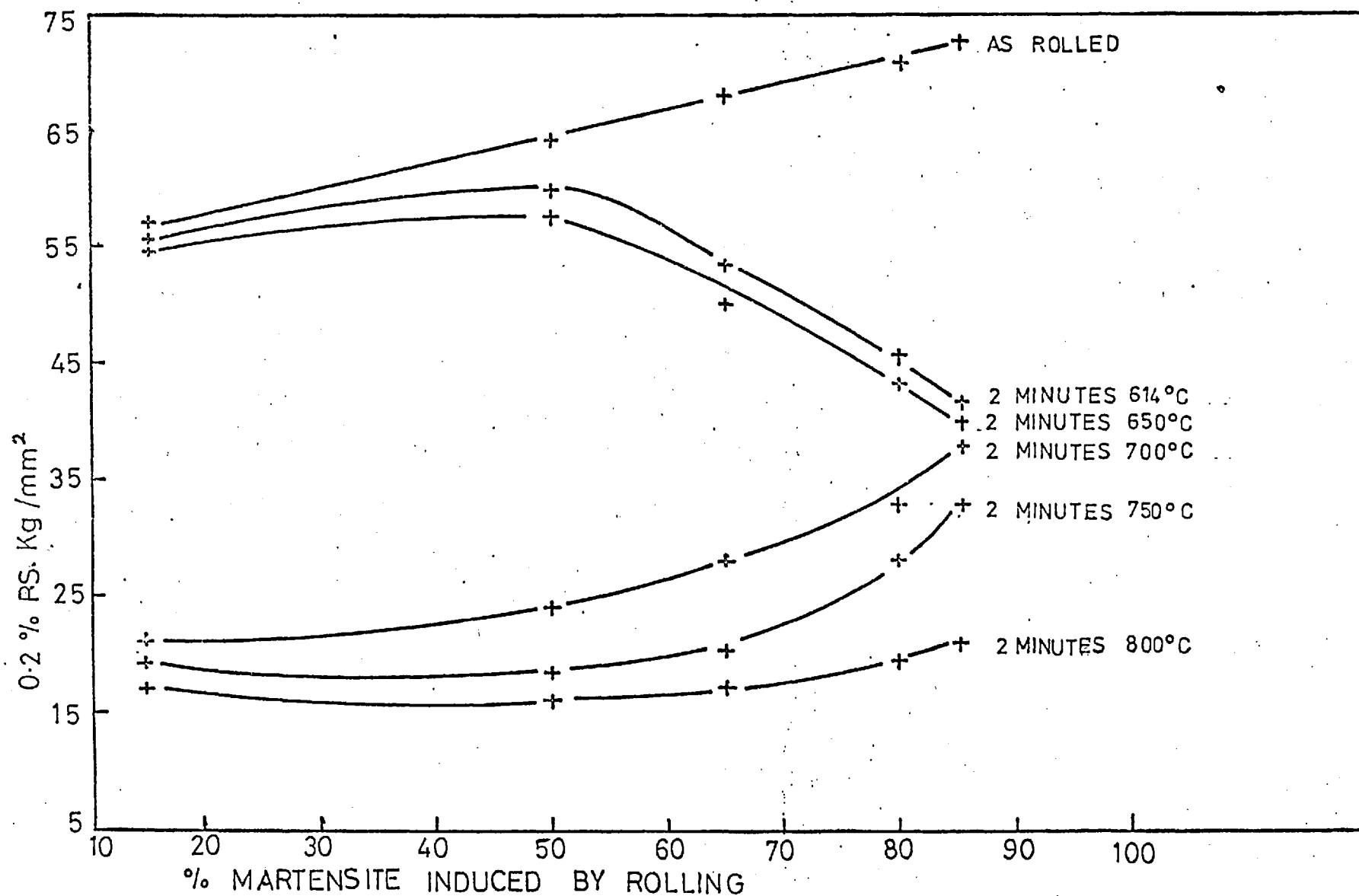


Fig. 6.8. Alloy A. Proof stress vs reversed austenite content for material deformed 50% at various temperatures and then heated for two minutes at various reversion temperatures

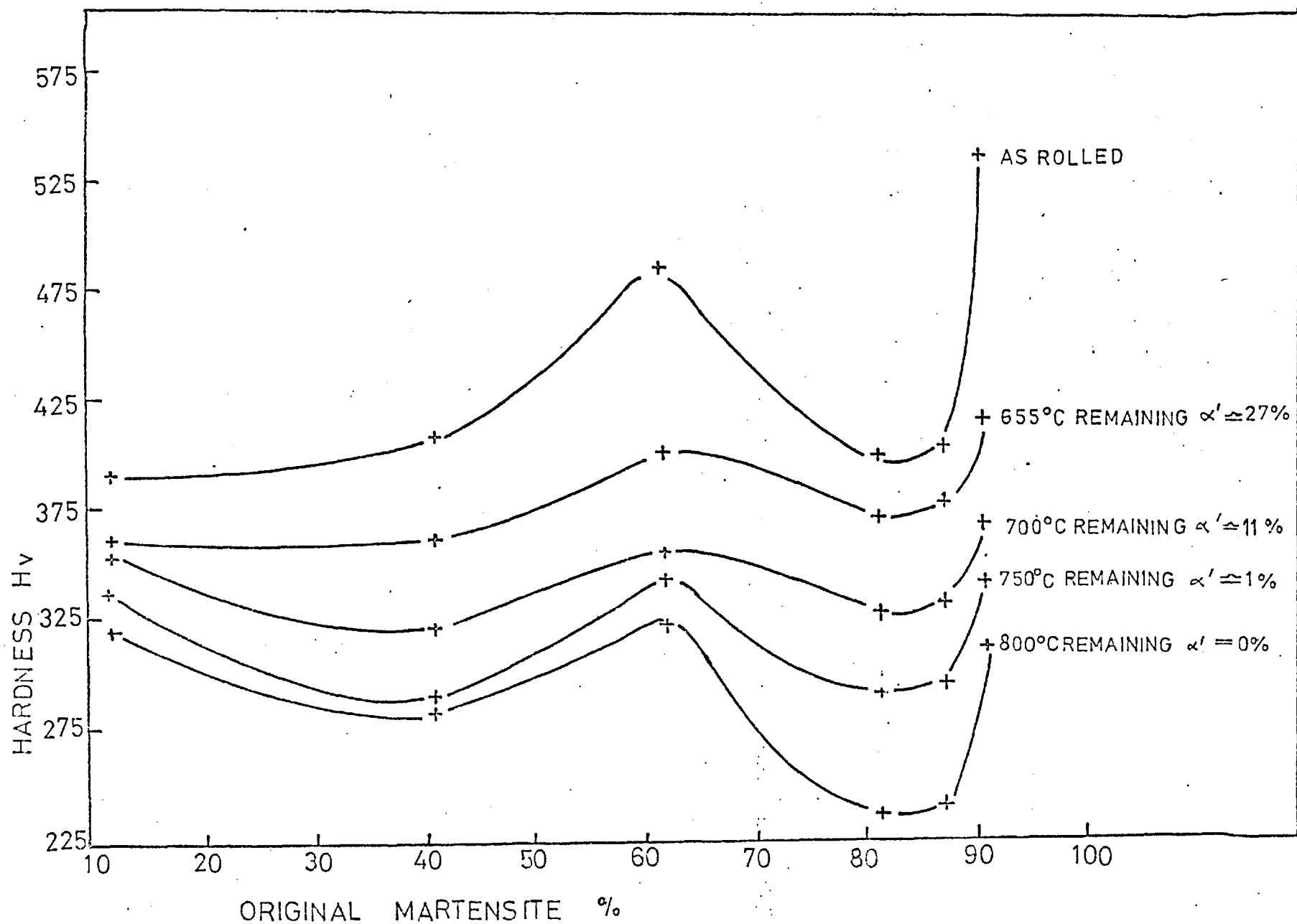


Fig. 6.9. Alloy B. Hardness vs martensite content after rolling, for material deformed 50% at various temperatures and then heated for two minutes at various reversion temperatures.

different from that at 800°C when the martensite was fully reverted. The general trend of the graphs in Fig. 6.9 follows the graph for the as rolled material (see Fig. 6.4) and differs from that of alloy A in two main features. Firstly, there was no sudden drop in hardness as was found between 650°C and 700°C in alloy A; and secondly there was a fall in hardness between specimens rolled at 20°C and those rolled at 0°C . It may also be noted that there was a small decrease in hardness with increasing reversed austenite content from 15% to 50%. The hardness of alloy B was higher than that of alloy A for all treatments.

A few tensile tests were performed in order to assess the ductility of these reversed structures. Alloy A, after 50% deformation at -78°C and two minutes at 700°C , had an elongation of 53% at fracture. The 0.2% proof stress was 31 kg/mm^2 and the U.T.S. 52 kg/mm^2 . Alloy B, after 50% deformation at -78°C and two minutes at 750°C , had an elongation of 34% at fracture. The 0.2% proof stress was 53 kg/mm^2 and the U.T.S. 133 kg/mm^2 .

6.1.5 Structural Aspects of Reversion.

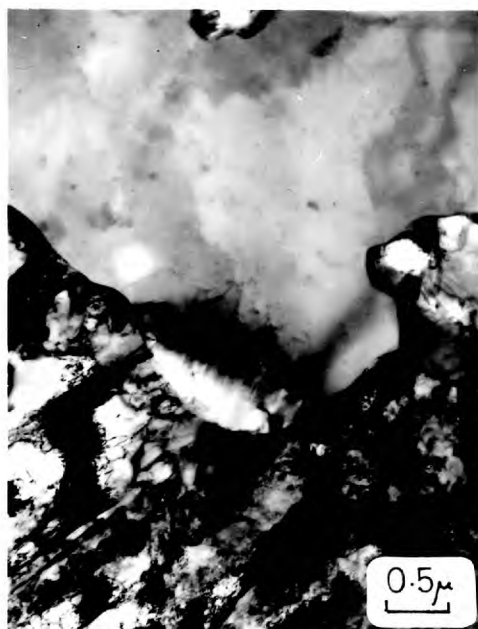
Figs. 6.10-6.16 show some of the structures associated with the reversion of deformation-induced martensite. Figs. 6.10-6.12 show structures of alloy A reversed for two minutes at various temperatures after rolling at -78°C . Fig. 6.10 shows the structure after two minutes at 600°C . The major part of the specimen contained a high dislocation density although a few areas were recrystallised as shown in Fig. 6.10.2. There is evidence in Fig. 6.10.1 of sub-grain formation. There was no sign of the twins found in specimens of reversed austenite formed from quench-induced martensite.

Fig. 6.11 shows structures formed after heating for two

Fig. 6.10



6.10.1. Alloy A. Rolled 50% at -78°C + 2 minutes at 600°C .



6.10.2. Alloy A. As 6.10.1.

Fig. 6.11



6.11.1. Alloy A. Rolled 50% at -78°C + 2 minutes at 700°C .



6.11.2. Alloy A. As 6.11.1.

minutes at 700°C. These were similar to those for the 600°C treatment but the sub-grain structure appeared more clearly developed. Fig. 6.11.1 shows an area of recrystallised structure adjoining an unrecrystallised area. Such recrystallised areas occupied a small proportion of the specimens. A lath-like appearance persisted in the unrecrystallised areas of Fig. 6.11.1 and sub-grains appeared to be forming across the laths. The top of Fig. 6.11.1 shows a region where sub-grain formation does not appear to have been well advanced. The sub-grain size in areas like Fig. 6.11.2 and the lath region of Fig. 6.11.1 was of the order of 0.5 to 2 μ .

Fig. 6.12 shows the structure after two minutes at 750°C. Fig. 6.12.1 shows two distinct ranges of grain size, the larger of which (approximately 4 μ in diameter) appears to consist of recrystallised grains, and the smaller of which (approximately 2 μ in diameter) appears to consist of sub-grains. The overall dislocation density in the sub-grain regions (e.g. Fig. 6.12.2) whilst still quite large, appeared somewhat lower than at the lower temperatures. Occasionally areas were seen in which an unrecrystallised grain was completely surrounded by recrystallised grains.

Figs. 6.13 - 6.16 show some structures of alloy B after reversion at various temperatures following 50% deformation at -78°C. Fig. 6.13 shows the structure after two minutes at 700°C. 90% martensite was produced by the rolling treatment and 11% remained after two minutes at 700°C. The structure still contained a high dislocation density although

Fig. 6.12



6.12.1. Alloy A. Rolled 50%
at -78°C + 2 minutes at
 750°C .



6.12.2. Alloy A. As 6.12.1.

Fig. 6.13.



6.13.1. Alloy B. Rolled 50%
at -78°C + 2 minutes at 700°C



6.13.2. Alloy B. As 6.13.1.

a sub-grain structure appeared to be beginning to form. There is some evidence of the sub-grains being contained in a lath structure in Figs. 6.13.1 and 6.13.2 although this is not very clear. No recrystallised areas were observed.

Fig. 6.14 shows the structure after two minutes at 750°C. There was much clearer evidence of sub-grain formation at this temperature, and the sub-grains appeared somewhat elongated in shape.. The sub-grains appeared to lie in bands, at least two directions of which are shown in Figs. 6.14.1 and 6.14.2. The sub-grain size was smaller than that in alloy A, being of the order of 0.1 - 0.5 μ . Fig. 6.14.1 indicates that not all the regions of the specimen had formed distinct sub-grains at this stage.

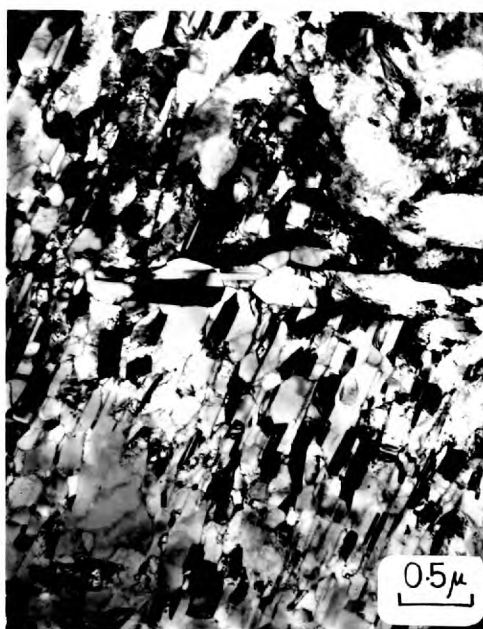
Fig. 6.15 shows the structure after two minutes at 800°C. Elongated sub-grains can again be seen, their size being somewhat larger than at 750°C. The dislocation density was still fairly high and no recrystallisation was observed.

In order to investigate the large strength decrease on increasing the reversion temperature from 650°C to 700°C for specimens of alloy A rolled at room temperature, structural observations were made of specimens reversed at 600°C and 700°C. The results are shown in Fig. 6.16. Fig. 6.16.1 shows the structure after two minutes at 600°C indicating that no recrystallisation had occurred, the dislocation density still being high. No clear cell structure was observed; however, since the as-rolled specimen only contained 15% martensite, this may simply have been missed. Fig. 6.16.2 illustrates the structure after two minutes at 700°C. At this temperature the specimen was almost fully recrystallised although a few

Fig. 6.14



6.14.1. Alloy B. Rolled 50%
at -78°C + 2 minutes at 750°C .



6.14.2. Alloy B. As 6.14.1.

Fig. 6.15

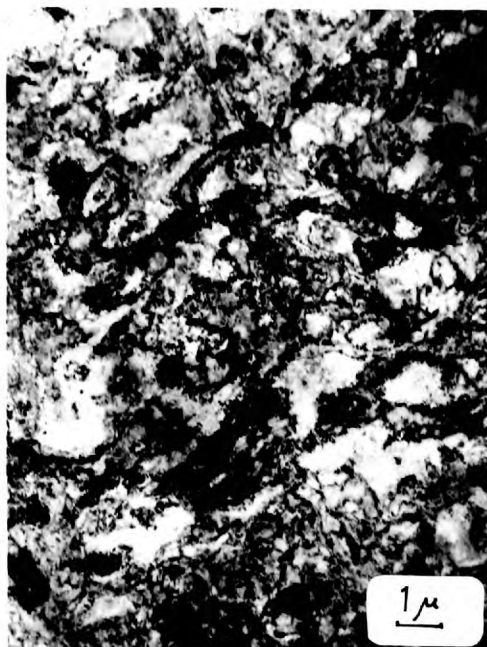


6.15.1. Alloy B. Rolled 50%
at -78°C + 2 minutes at 800°C .



6.15.2. Alloy B. As 6.15.1.

Fig. 6.16.



6.16.1. Alloy A. Rolled 50%
at room temperature + 2
minutes at 600°C.



6.16.2. Alloy A. Rolled 50%
at room temperature + 2
minutes at 700°C.

Fig. 6.17



6.17.1. Alloy B. Rolled 50%
at room temperature + 2 minutes
at 700°C.



6.17.2. Alloy B. As 6.17.1.

dislocated areas were observed e.g. Fig. 6.16.2.

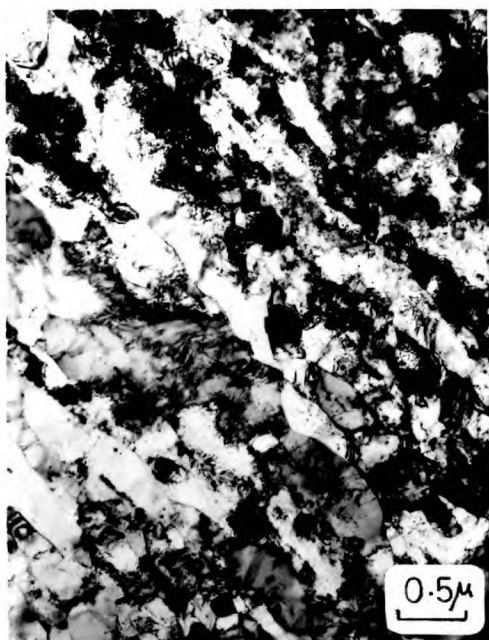
Similar experiments were performed with alloy B and the results are illustrated in Figs. 6.17 and 6.18 for reversion temperatures of 700°C and 750°C respectively. In contrast to alloy A no evidence was found of recrystallisation, although Fig. 6.17.2 shows some evidence of its starting. Some areas, e.g. Fig. 6.17.1, were essentially unchanged by the heat treatment, whilst others e.g. Figs. 6.17.2, 6.18.1 and 6.18.2, showed evidence of sub-grain formation as was observed for the material rolled at -78°C for these reversion temperatures.

In order to establish how quickly the structures described above could form, some specimens were rolled at -78°C and then reversed for 14 seconds at 900°C . In alloy A this treatment resulted in almost complete recrystallisation, but in alloy B a sub-grain structure was observed similar to those seen after two minutes at lower temperatures; this is illustrated in Figs. 6.18.3 and 6.18.4. The dislocation density remained high.

6.1.6 Recovery and Recrystallisation.

The recovery and recrystallisation characteristics of the structures described above were investigated using alloy A. Specimens were used which had been rolled at room temperature or -78°C . The decrease in hardness with increasing time at 700°C is shown for both rolling temperatures in Fig. 6.19. The initial fall in hardness, on reversion for 30 seconds, was greater for the specimens rolled at -78°C than for those rolled

Fig. 6.18



6.18.1. Alloy B. Rolled 50%
at room temperature + 1 minute
at 750°C.



6.18.2. Alloy B.
As 6.18.1.



6.18.3. Alloy B. Rolled 50%
at -78°C + 14 seconds at
900°C.



6.18.4. Alloy B.
As 6.18.3.

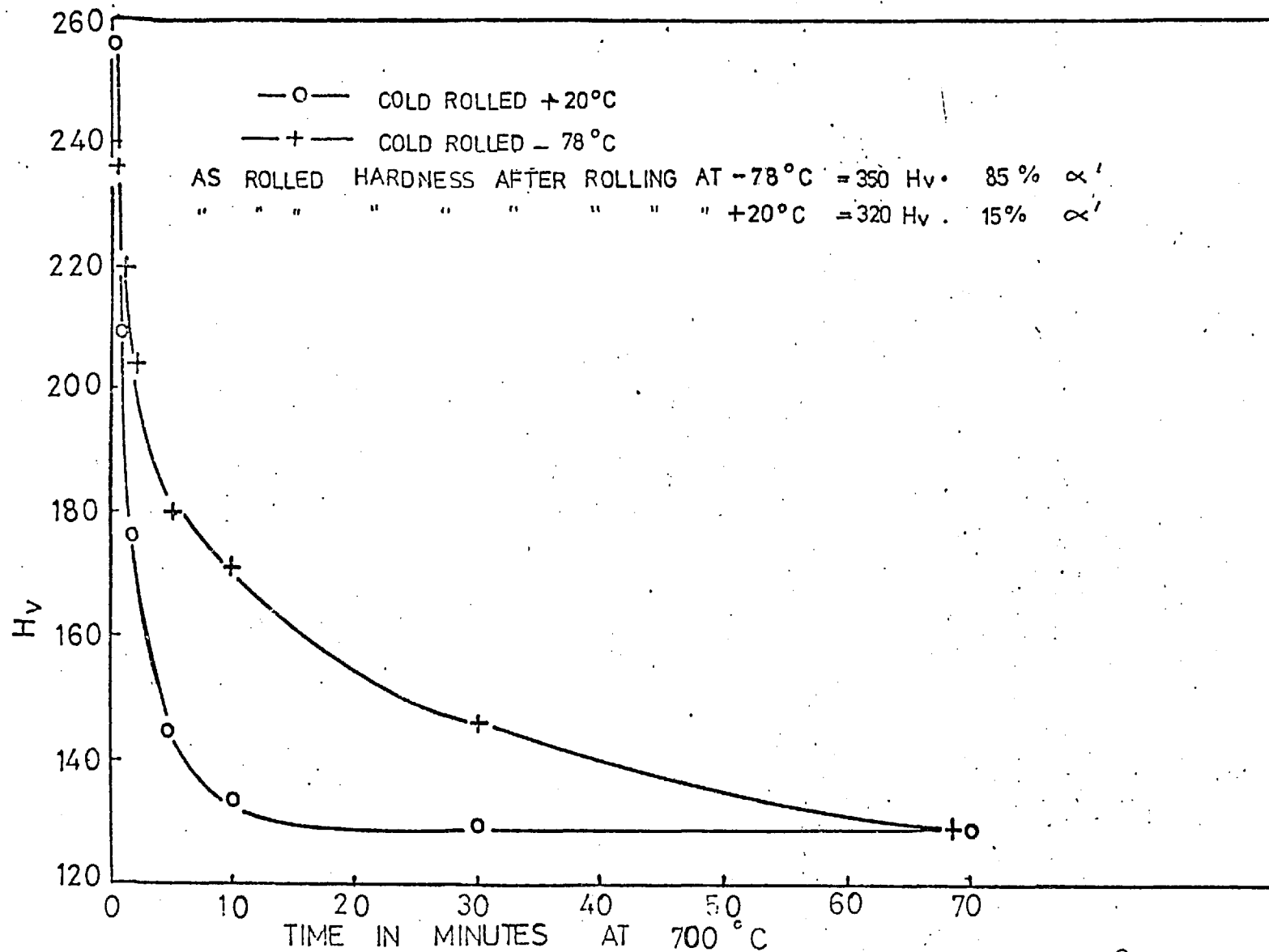


Fig. 6.19. Alloy A. Hardness changes during isothermal holding at 700°C of specimens deformed 50% at room temperature and -78°C.

at room temperature, but subsequently the hardness of the room temperature rolled specimens fell more rapidly than those rolled at -78°C . The fall in hardness was complete after about ten minutes for the specimens rolled at room temperature, but continued up to about 70 minutes for those rolled at -78°C . The final hardness was the same in both cases.

Some of the structures developed in these specimens during recovery and recrystallisation were investigated by electron microscopy. The structures after two minute reversion treatments have been illustrated previously in Figs. 6.11 and 6.16.

Figs. 6.20 and 6.21 show the structures of material rolled at -78°C and then held for 10, 20 and 35 minutes at 700°C . Fig. 6.20.1 shows that part of the specimen had completely recrystallised after 10 minutes at 700°C . This partial recrystallisation was also seen after two minutes at 700°C (see Fig. 6.11) but the grain size appeared somewhat larger after ten minutes. Figs. 6.20.2 and 6.20.3 show what seems to be the beginning of recrystallisation in the areas which had formed sub-grains and not yet recrystallised. Fig. 6.20.2 shows a recrystallised grain, on the left of the micrograph, which still appears to have a low angle boundary (arrowed) with the dislocated grain below it. Fig. 6.20.3 shows two grains, near the bottom of the micrograph, which seem to be recrystallised but still contain some dislocations (arrowed) in the configuration of low angle boundaries.

Fig. 6.20.4 shows the structure of material rolled at -78°C after 20 minutes at 700°C . Once again large areas were completely recrystallised, and recrystallised grains also

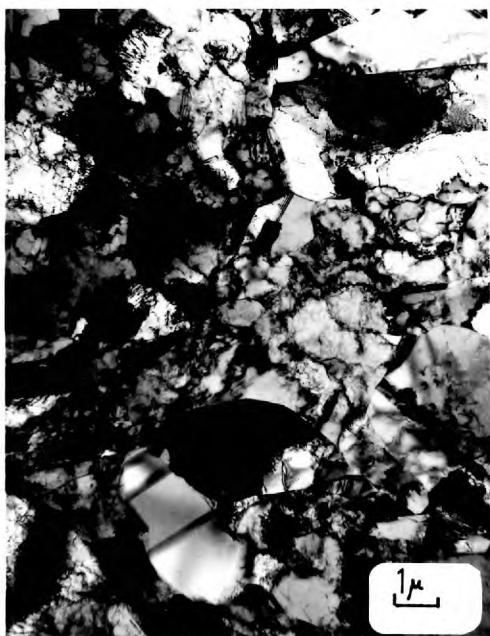
Fig. 6.20



6.20.1. Alloy A. Rolled
50% at -78°C + 10 minutes
at 700°C .



6.20.2. Alloy A.
As 6.20.1.



6.20.3. Alloy A.
As 6.20.1.



6.20.4. Alloy A. Rolled 50%
at -78°C + 20 minutes at
 700°C .

appeared inside the sub-grain areas. These new, recrystallised grains were generally very small, although a relatively large one is shown in Fig. 6.20.4, in the bottom left hand corner. Fig. 6.21.1 shows the structure after 35 minutes at 700°C ; the completely recrystallised regions extended throughout most of the specimen at this stage, although some dislocation debris remained.

During the course of the work on the isothermal reverse martensite transformation, the diffusional transformation of martensite to austenite in deformed material was investigated at 520°C (below the A_s). Fig. 6.21.2 shows the structure of alloy A, rolled at -78°C and held for 10,000 minutes at 520°C . The material contained 11% ferrite; however, a sub-grain structure similar to that found in shorter times at higher temperatures, can be seen in Fig. 6.21.2, and also a number of small, recrystallised grains of the order of $0.5 - 4 \mu$ in diameter.

Reversed, deformation-induced martensite was found to cause considerable stabilisation of the austenite produced. Less than 3% martensite was produced on quenching to -196°C the structures produced by rolling either alloy at -78°C and reversing for two minutes at 700°C . Re-rolling alloy A 50% at -78°C , after the initial rolling at -78°C and reversion at 700°C , produced 56% martensite as compared with 85% on the first rolling. The structure produced by this re-rolling is illustrated in Fig. 6.22.1. The structure was very heavily dislocated as was the initial rolled structure, but the second rolling appeared to produce a less obviously lath-like structure. The hardness of this material was

Fig. 6.21



6.21.1. Alloy A. Rolled 50%
at -78°C + 35 minutes at
 700°C .

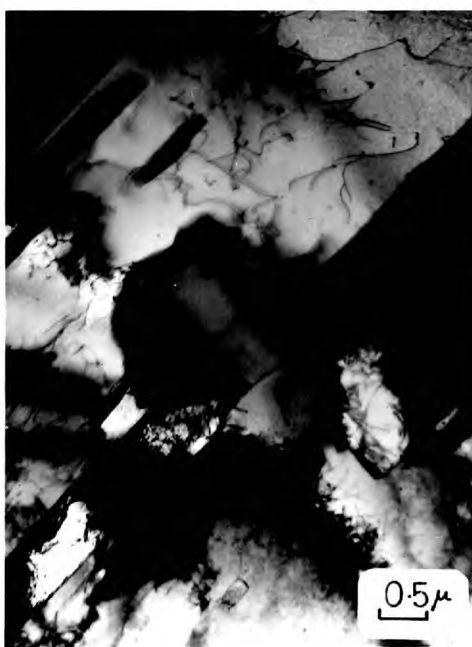


6.21.2. Alloy A. Rolled 50%
at -78°C + 7 days at 520°C .

Fig. 6.22



6.22.1. Alloy A. Rolled 50%
at -78°C + 2 minutes at 700°C
+ re-rolled 50% at -78°C .



6.22.2. Alloy A. As 6.22.1.
+ 2 minutes at 700°C .

552 Hv as compared with 538 Hv on the first rolling.

Fig. 6.22.2 shows a structure resulting from reversion of this re-rolled material. Some evidence could be seen of elongated sub-grains such as were found after the first reversion, and, indeed, the general structure was quite similar to that shown in Fig. 6.11, but the sub-grains appeared somewhat larger and less well defined after the second reversion.

6.1.7 Textures.

Figs. 6.23 - 6.25 show the $\{110\}$ pole figure for martensite produced by 50% deformation of alloy A at -78°C , and the $\{111\}$ austenite pole figures for the same specimen after two minutes and two hours at 700°C .

The martensite texture shown in Fig. 6.23 is fairly typical of a $\{110\}$ pole figure for deformed b.c.c. material⁽¹¹²⁾. The austenite pole figures in Figs. 6.24 and 6.25 are also more typical of rolling textures than recrystallisation textures. They resemble the copper rolling texture as shown by Hu et al⁽¹¹³⁾ for 96% rolled copper. Hu and Beck⁽¹¹⁶⁾ also found that this texture could be 'retained', in certain f.c.c. alloys, after recrystallisation.

These pole figures may only be used to obtain indications of the textures of the specimens. In order to obtain a full understanding of the textures the other regions of the pole figures would need to be determined using the, time-consuming, transmission method. Also other pole figures would need to be determined. There was not time in this project for this work to be completed, nor was it really necessary for the purposes of the investigation.

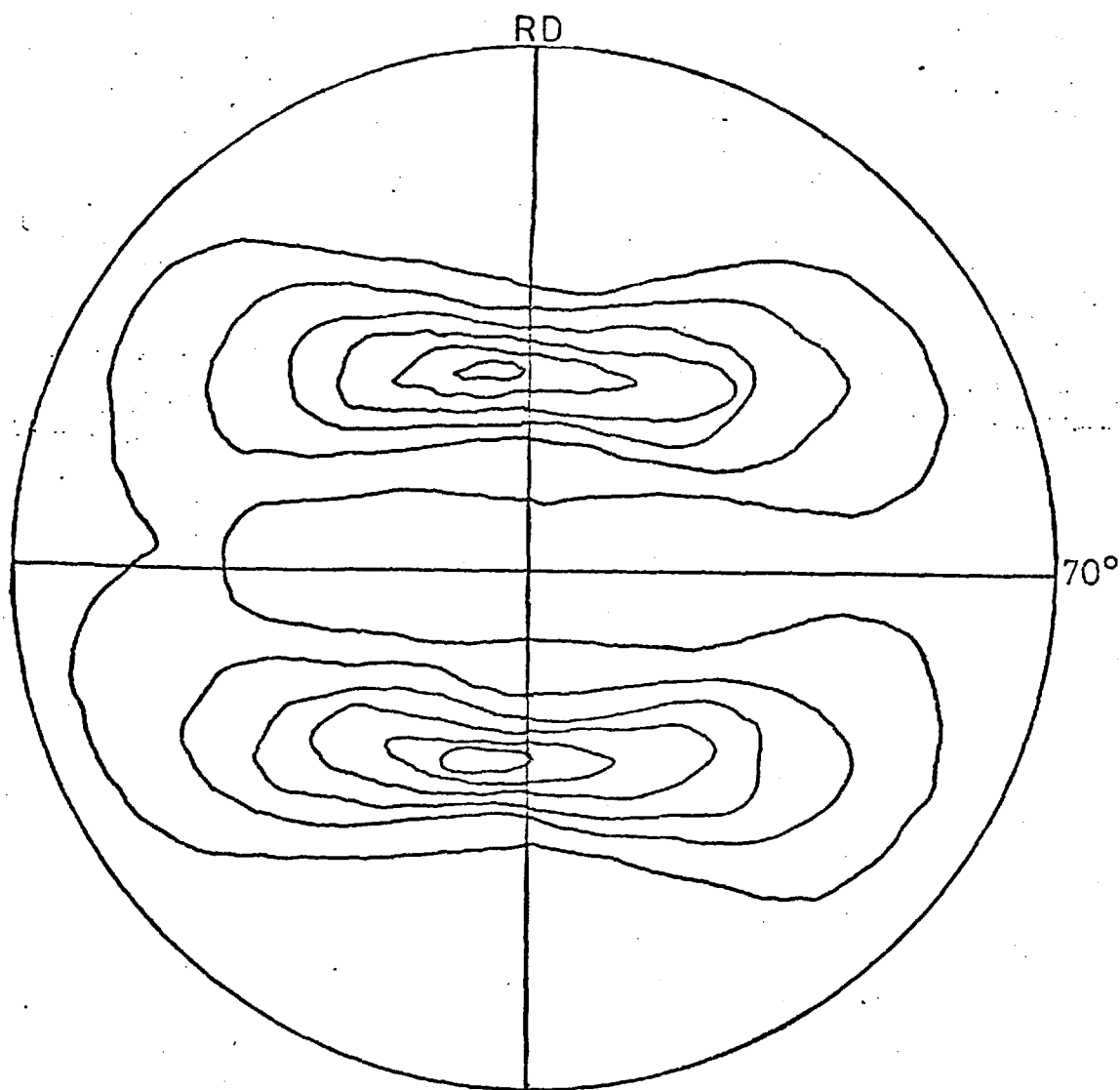


Fig. 6.23. Alloy A. 50% deformed at -78°C

{110} Martensite Pole Figure.

The specimen contained 85% martensite.

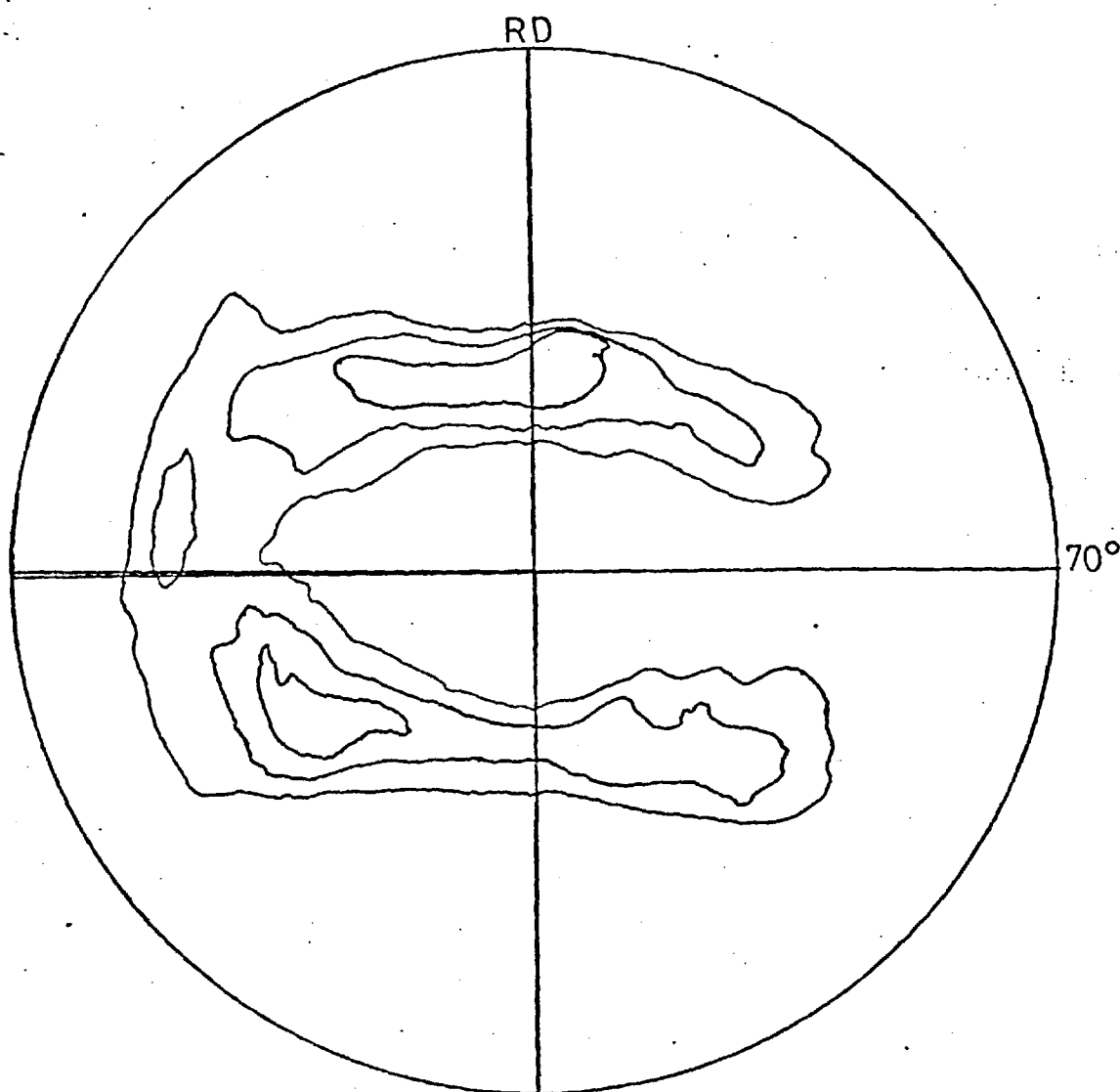


Fig. 6.24. Alloy A. 50% deformed at -78°C + heated for two minutes at 700°C . Same specimen as used for Fig. 6.23.

. {111} Austenite Pole Figure.

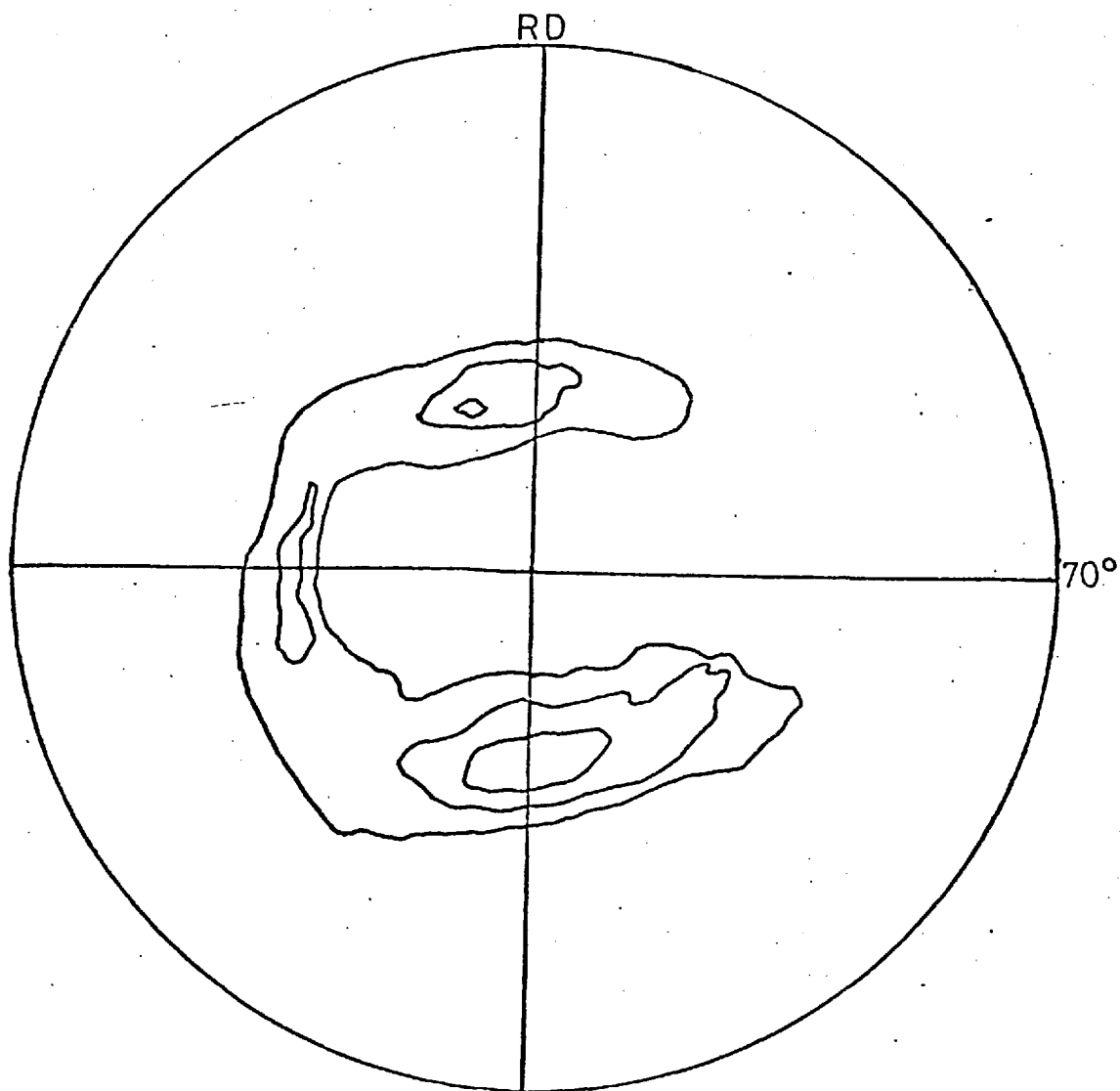


Fig. 6.25. Alloy A. 50% deformed at -78°C + heated for two hours at 700°C . Same specimen as used for Figs. 6.23 and 6.24.

{111} Austenite Pole Figure.

6.2 DISCUSSION.

6.2.1 The Direct Transformation.

It was mentioned in section one that other workers^(7,68) have observed that deformation produces a lath martensite similar in structure to quench-induced martensite. This is confirmed for the present alloys in Figs. 6.1 and 6.2. Fig. 6.2.1 shows a $\{111\}_\gamma$ orientated foil in which the laths lay at 60° to each other. This corresponds to the observation by Breedis⁽⁸⁾ that quench-induced laths of martensite lie parallel to $\{111\}_\gamma$ planes with the long directions of the laths parallel to $[110]_\gamma$. The fact that Fig. 6.3.3 shows laths in the transverse section indicates that the laths were not aligned parallel to the rolling direction.

Since the martensite was produced by 50% deformation at various temperatures, there are several mechanisms which need to be taken into account when considering the strengthening aspects of the transformation.

- 1) Deformation of the retained austenite. Lowering the deformation temperature increases the work hardening rate of austenite although the yield stress is virtually unaffected.⁽¹¹⁴⁾
- 2) The formation of martensite. The martensitic transformation may be regarded as a competing process with plastic deformation⁽¹¹⁵⁾ and the amount of martensite produced may, therefore, affect the work hardening produced.
- 3) Deformation of the martensite. The rolling was carried out in several passes and, therefore, any martensite produced during the first pass would be deformed during subsequent

passes. The temperature may have affected this process in two ways. Firstly, the lower the temperature, the earlier the martensite may have formed; and the earlier the martensite formed, the more deformation it would have received. Secondly,

lowering the deformation temperature of the martensite increases the yield stress but does not markedly affect the work hardening rate.^(114,117) The magnitude of this effect increases with decreasing temperature. The overall effect of deformation temperature is greater for martensite than for austenite.

4) Strain-Ageing. In alloy B, at temperatures above room temperature, some redistribution of carbon is likely. Although the deformation temperatures were too low to expect dynamic strain-ageing⁽¹¹⁸⁾ (except, possibly at 150°C), fairly rapid static strain-ageing could have occurred above room temperature. Owen and Roberts⁽¹¹⁹⁾ found static strain-ageing to occur within minutes at room temperature in an Fe - Ni - C martensite.

5) The comparative strengths of martensite and austenite. Martensite is generally expected to be stronger than austenite due to its b.c.c. structure as compared with the f.c.c. austenite.

The linear relationship between proof stress and percentage martensite observed for alloy A (see Fig. 6.4) is similar to that observed by Mangonon and Thomas⁽⁶⁸⁾ in an 18/8 stainless steel. These workers concluded that the strengthening by the martensite was due to the composite structure; this was discussed in the previous chapter. In the present case, there is an additional complication due

to the martensite being induced by rolling at different temperatures, whilst Mangonon and Thomas varied the deformation at a standard temperature of -196°C . Since the strengthening effect of deformation on both martensite and austenite increases with decreasing temperature it is rather surprising to find the graph of proof stress against percentage martensite, linear. Possibly the strengthening effect of the presence of the martensite decreased with increasing martensite, as was observed for up to 70% quench-induced martensite in an Fe - Ni alloy by Gorbach and Malyshev⁽³⁶⁾; whilst the strengthening effect of deformation increased with decreasing temperature and, therefore, increasing martensite. These two effects may then have cancelled out to give a linear result. Fig. 6.5 indicates a small peak in ductility, in tension, when deforming alloy A at about 0°C , presumably due to transformation plasticity. This may have affected the strength after rolling. However, if the plasticity in tension were due to martensite forming at any incipient necks⁽¹¹⁵⁾ and so preventing necking, this mechanism would not apply during rolling. Also, it must be remembered that the high strain rate on rolling caused a temperature rise of about 30°C and this would have affected the position of the ductility peak, as would the fact that rolling is essentially a compression process and not tension.

In alloy B there are several extra factors to be considered. Firstly, the higher carbon content allowed the possibility of strain-ageing. Secondly, the ductility peak in tension, shown in Fig. 6.6, was much larger, and at a higher temperature than in alloy A. Thirdly, the

strengthening effect of carbon on austenite and martensite must be considered, although the strengthening increment produced by quench-induced martensite in alloy B was not found to be higher than in alloy A.

At no stage was the hardness vs percentage martensite graph for alloy B, shown in Fig. 6.4, linear. The M_d of alloy B was much higher than alloy A although the M_s temperatures were similar, and a similar amount of martensite was produced by rolling at -78°C . The strengthening effect of deformation-induced martensite was apparently greater in alloy B than in alloy A.

The increased strength of alloy B over alloy A at the higher temperatures may have been due to strain-ageing in the martensite in alloy B. The strain-ageing would have occurred in the martensite and not in the austenite due to the faster diffusion of carbon in a b.c.c. structure. Hardness measurements failed to detect any strain-ageing within an hour after rolling 50% at room temperature. but the temperature during rolling may have risen enough to allow some strain-ageing to occur between passes. The higher strengthening increment per percent martensite for alloy B may also have been associated with the fact that, due to the higher M_d in alloy B, the temperature differences between points on the graph in Fig. 6.4 were greater for alloy B than for alloy A.

The fall in hardness between room temperature and 0°C rolling in alloy B may also have been due to strain-ageing, since strain-ageing may have occurred between passes at room temperature and above, but not at 0°C and below due to the

slower diffusion rates. This suggestion is supported by the observation that the increased strength of alloy B over alloy A was very similar at 15% martensite, where strain-ageing was restricted by the small amount of martensite, and at 80% martensite where the temperature may have been too low for strain-ageing.

One other possible cause for the decrease in hardness at 0°C rolling for alloy B, is that continuous transformation may have restricted plastic deformation. The ductility peak in tension appeared at a high temperature, but, as discussed earlier, this peak may have been due to different reasons, i.e. martensite formation at necks in tensile test pieces, and also may have been affected by the faster strain rate and compressive conditions of rolling. Fig. 6.26 shows that the slope of the graph of percentage martensite against rolling temperature for alloy B, appeared to increase between room temperature and 0°C, thus supporting the possibility of a peak in transformation plasticity in this temperature range.

Fahr⁽¹¹⁵⁾ separated deformation-induced martensite into two categories: (1) Strain-induced martensite which forms after plastic deformation of the austenite; and, (2) stress-induced martensite which forms before any plastic deformation of the austenite due to the higher driving force for the martensitic transformation. It is possible that the change over between these two types in alloy B occurred between room temperature and 0°C and this may also have affected the strength.

Between ^{rolling at} -20°C and -78°C rolling, in alloy B, there was a

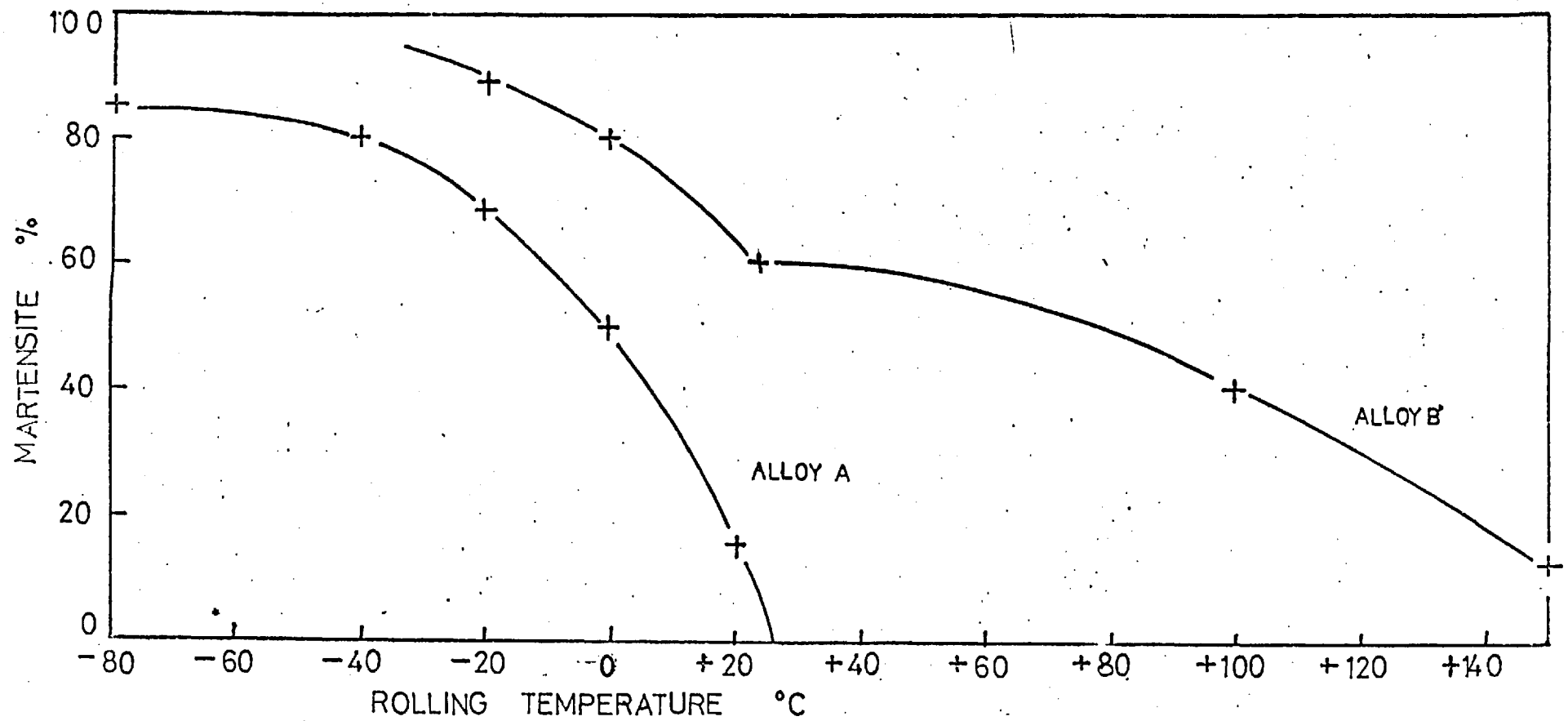


Fig. 6.26. The amount of martensite produced by 50% deformation at various temperatures.

large increase in strength without a large increase in martensite content. This effect was probably due to the rolling temperature, but may also have been linked with the stage of rolling at which the martensite formed. -78°C was below the M_s and so, probably, the martensite formed earlier in the deformation than at -50°C . Thus, the final martensite would have been work-hardened more at -78°C which would have caused an increase in strength.

The non-linearity of the hardness graph for alloy A in Fig. 6.4 as compared with the proof stress curve was probably due to an increased work hardening rate with increasing martensite content.

In order to establish the mechanisms involved in strengthening by deformation-induced martensite, a much fuller investigation than that performed here is obviously required. This discussion, however, has outlined some of the possible mechanisms involved and these ideas are also utilised in examining the reversed structures.

6.2.2 The Reverse Transformation.

The A_s and A_f temperatures were found to be the same for quench-induced and deformation-induced martensite. This was in contrast to the effect of deformation of austenite on the M_s , since other workers^(84,95) have found the M_s to decrease with increasing austenite yield strength. The reason suggested⁽⁸⁴⁾ for the decrease in the M_s was that the strain energy associated with the transformation was higher in a stronger matrix. The implication, therefore, is that the

strain energy does not play as large a part in the reverse transformation as in the direct transformation. The reason for this may be that dislocation movement is easier at the higher temperatures required for the reverse transformation.

Fig. 6.7 shows a large drop in hardness, for specimens of alloy A. on increasing the reversion temperature from 650°C to 700°C , especially for specimens containing less than 50% martensite after rolling. The reason for this decrease was determined by structural work illustrated in Fig. 6.16. This figure shows that, for specimens rolled 50% at room temperature, a two minute reversion at 600°C resulted in no recrystallisation (Fig. 6.16.1), whilst a two minute reversion at 700°C resulted in a largely recrystallised structure (Fig. 6.16.2). Similar micrographs for specimens deformed at -78°C , shown in Figs. 6.10 and 6.11, indicate that very little recrystallisation had occurred even after two minutes at 700°C although small recrystallised areas could be seen at this temperature. Thus, it seems that two minute treatments at 600°C , and, presumably, 650°C , were not sufficient to cause any recrystallisation. Two minutes at 700°C or above, however, resulted in considerable recrystallisation of the room temperature deformed material. From the proportions of recrystallised to unrecrystallised structure, it seems likely that the retained austenite had recrystallised but the reversed austenite had not. This recrystallisation, therefore, caused the fall in hardness between 650°C and 700°C reversion treatments.

Figs. 6.7 and 6.8 show a peak in hardness and proof stress at about 50% reversed austenite for specimens of

alloy A which had been reversed at 600°C and 650°C . The reasons for this peak were probably connected with the deformation characteristics and the recovery characteristics of the martensite and austenite. The work hardening rate of austenite increases with decreasing deformation temperature⁽¹¹⁴⁾. Thus, the lower the deformation temperature, the stronger the retained austenite would have been. Fig. 6.19 shows that, after 30 seconds at 700°C , a specimen rolled at -78°C and containing 85% reversed austenite was softer than one rolled at room temperature and containing 15% reversed austenite. Thus, it seems that recovery in reversed austenite occurred faster than in retained austenite, resulting in reversed austenite being softer than retained austenite after recovery but not recrystallisation had occurred. Thus, it seems that, for two minute reversions at 600°C and 650°C , the strength of the retained austenite increased with decreasing deformation temperature, but the strength of the reversed austenite was lower than that of the retained austenite due to more recovery having taken place. The actual strength of the reversed austenite may have increased with decreasing deformation temperature due to earlier formation, and therefore greater deformation, of the martensite. Therefore, adding the fact that decreasing temperature of deformation increased the strength of retained and, possibly, reversed austenite, to the fact that increased recovery caused the reversed austenite to be softer than the retained austenite, resulted in the temperature effect being dominant up to 50% reversed austenite and the strength increasing, but, when the structure contained more than 50% reversed austenite, the

strength decreased due to the greater proportion of the softer phase.

When reversion was carried out at 700°C and above, it has been demonstrated that the retained austenite recrystallised, whilst the reversed austenite formed sub-grain regions. Thus, at these temperatures, the retained austenite was very low in strength and so, in all cases, an increase in the reversed austenite content resulted in an increase in strength. However, it may be seen in Figs. 6.7 and 6.8 that for an increased reversed austenite content from 15% to 50% very little increase in strength occurred. This phenomenon may be linked with the preceeding observations in that later formation, and, therefore, lower deformation, of the martensite formed at room temperature, may have resulted in the sub-grain formation, which is observed on reversion for specimens deformed at lower temperatures, not occurring. This would have increased the strength of the reversed, room-temperature deformed specimens with respect to those deformed at lower temperatures. This possibility is supported by the structural observations since Fig. 6.16.2 shows a region of more heavily deformed structure after reverting a specimen deformed at room temperature for two minutes at 700°C , than the structures shown in Fig. 6.11 for similar reversions of specimens deformed at -78°C .

The graphs in Fig. 6.9 showing the variation in hardness of alloy B with the amount of reversed austenite produced at different temperatures, follow closely the general form of the hardness vs martensite content graph for that alloy shown in Fig. 6.4. It seems likely, therefore, that the reversed

austenite inherited the basic features of the martensitic structure. Thus, whatever the reason for the decrease in hardness between room temperature rolling and rolling at 0°C , be it strain-ageing, transformation plasticity, or some other factor, the reversed austenite appeared to inherit the effect of the resultant structural features. This presumably means, in the case of strain-ageing, that the dislocations remained pinned during reversion, or, in the case of transformation plasticity, that the dislocation density remained relatively low.

There was no evidence of a large drop in hardness between two reversion temperatures for alloy B such as was found between 650°C and 700°C in alloy A. Figs. 6.17 and 6.18 show micrographs of alloy B, originally rolled at room temperature (producing 40% martensite), after reversion for two minutes at 700°C and 750°C . There was no evidence of recrystallisation of the retained austenite, and the generally high hardness levels after reversion, (see Fig. 6.9) confirm that the retained austenite in alloy B did not recrystallise on reversion for two minutes even at 800°C . This slower recrystallisation in alloy B as compared with alloy A may have been due to the generally higher temperatures of deformation of alloy B causing less work hardening of the austenite. Alternatively, alloy B may have had a higher stacking fault energy than alloy A (this is supported by the fact that the M_d was higher in alloy B⁽¹¹⁵⁾) which may have resulted in slightly different deformation characteristics.

The decrease in strength resulting from reversion in alloy B increased with increasing initial martensite content

up to 60% martensite. This was presumably due to the reversed austenite recovering faster than the retained austenite as was observed in alloy A. The decrease in strength on reversion then decreased for specimens rolled at 0°C and -20°C , presumably due to lack of strain-ageing effects or lower initial dislocation density due to transformation plasticity, and then rose again for specimens rolled at -78°C , presumably due to the very high work hardening of the martensite at this temperature.

6.2.3 Recovery and Recrystallisation.

Fig. 6.19 shows the decrease in hardness with increasing time at 700°C for specimens of alloy A cold rolled at room temperature or -78°C , containing 15% or 85% martensite respectively. The initial fall in hardness was greater for the material rolled at -78°C than for that rolled at room temperature, but the room temperature material then softened much more rapidly than that containing the larger amount of martensite.

The two processes which result in softening of material held at a relatively high temperature, recovery and recrystallisation; both have the same driving force, viz; the difference in free energy between deformed and undeformed material. The distinction between the two processes is generally taken to be⁽⁹⁶⁾ that recovery constitutes all the processes which occur before the appearance of a new, strain-free grain with high angle boundaries; and recrystallisation comprises the nucleation and growth of new, strain-free grains involving the consumption of deformed material by the

movement of high angle boundaries through it.

The softening of material on annealing exhibits a different time dependence according to whether recovery or recrystallisation is involved.⁽⁹⁶⁾ During recovery softening is most rapid at short times, the rate decreasing exponentially with time. No incubation period is required for recovery. An incubation period is however exhibited by recrystallisation processes, after which softening occurs very rapidly. The graph for the material rolled at -78°C in Fig. 6.17 exhibits a form more consistent with recovery processes than with recrystallisation, whilst the material rolled at room temperature softened so rapidly that recrystallisation is indicated even though the incubation period was very short.

The structural evidence confirms the above ideas. The major part of the material originally rolled at room temperature was completely recrystallised after two minutes at 700°C . Whereas the material originally rolled at -78°C contained only small recrystallised areas after two minutes at 700°C , the major part of the specimen still being heavily deformed, although a sub-grain structure appeared to be forming. The proportions of recrystallised to unrecrystallised grains in these two types of material led to the conclusion that the deformed, retained austenite had recrystallised after two minutes at 700°C , but the previously martensitic areas had not recrystallised.

Fig. 6.11.1 indicates that sub-grains formed in the previously martensitic areas across the previous laths. The sub-grains formed were approximately the same diameter as the

individual martensitic crystals formed by the original deformation (See Fig. 6.1) and it seems possible therefore, that the boundaries of the sub-grains were those of the original martensite crystals. Increasing the temperature of reversion (See Figs. 6.10 - 6.12 and 6.13 - 6.15) made the sub-grains more distinct but did not increase their size markedly for the two minute treatments.

Figs. 6.20 and 6.21 show some structures of the material rolled at -78°C , after longer times at 700°C . An increasing amount of recrystallised structure was found with increasing time at 700°C , and also recrystallised grains were observed to form in the sub-grain regions, e.g. Figs. 6.18.2, 6.18.3 and 6.18.4. Thus, it appears that recrystallisation did occur in the reversed martensite regions but at a later stage than in the retained austenite regions. The increasing amount of fully recrystallised material with increasing time indicates that the recrystallised, retained austenite grew into the unrecrystallised reversed austenite. This conclusion is further indicated by the fact that room temperature rolled material was fully recrystallised after approximately 15 minutes at 700°C at which time the reversed austenite in the material deformed at -78°C was not recrystallised. Therefore, the reversed austenite in the room temperature deformed material may have recrystallised faster than in the other specimens; this is consistent with the earlier suggestion that the sub-grain formation might not occur so readily in this material. Alternatively the recrystallised retained austenite may have grown into the reversed austenite, eventually enveloping it entirely. This mechanism has been observed before in Fe - Ni alloys by Zaytsev and Gorbach⁽⁵⁷⁾

It still remains to discuss why the reversed austenite appears to recrystallise more slowly than the retained austenite. It will be helpful to consider briefly at this point the main theories so far propounded for nucleation in recrystallisation.

Firstly, there is the classical nucleation model first formulated by Becker⁽⁹⁹⁾. This model is based on the idea of a nucleus forming by the random diffusion of a group of atoms causing them to come together in such a configuration as to form an embryo recrystallised grain. This embryo then grows or disperses, depending on the balance between its surface energy, favouring dissipation, and its volume free energy, favouring growth. Calculations of the activation energy for recrystallisation to nucleate by this means have produced figures which are too large to make it feasible.

Secondly, there is the bulge nucleation model. This model, originally proposed by Bailey and Hirsch⁽⁹⁸⁾, derives the driving force from a difference in dislocation density between two adjacent grains. If this difference exists and certain other energy requirements are fulfilled, the grain boundary will tend to bulge into the more heavily dislocated grain, leaving behind it a relatively dislocation-free region.

Thirdly, there is a model involving the formation of sub-grains, followed by growth or coalescence of some of the sub-grains until a recrystallised grain is formed. This mechanism was first proposed in a general way by Cahn⁽¹⁰⁰⁾ and Beck⁽¹⁰¹⁾, and later demonstrated in Fe - 3% Si alloys by Hu⁽⁹⁴⁾ and Walter and Koch⁽¹⁰²⁾. Walter and Koch simply proposed that one or more of the sub-grains would act as an embryo recrystallised grain and grow into the matrix, whilst

Hu suggested that sub-grains coalesced, postulating that neighbouring grains rotated until the boundary between them disappeared.

In the present work there is evidence to suggest that the austenite reversed after deformation recrystallised by the sub-grain growth or coalescence mechanism. The formation of sub-grains in reversed austenite areas is quite clear from many of the micrographs, and also there is evidence of recrystallised grains within the sub-grain regions in Figs. 6.20.2, 6.20.3 and 6.20.4. The size of the sub grains was of the same order as those described by Hu and by Walter and Koch. The misorientations of the sub-grains have been found to be of the order of 5° , those of Hu being 4° or less. The small misorientations may have arisen as a result of the reverse martensite transformation, since, in quenched material, it has been shown⁽¹⁾ that reversed austenite grains in alloy A returned to almost the same orientation as the original, solution treated, austenite. There are indications in Fig. 6.20.2 and 6.20.3 that the recrystallizing grains contained within them the remains of low angle boundaries (arrowed) similar to those described by Hu. Thus, it is possible that the reversed austenite recrystallised by a sub-grain coalescence mechanism.

Additional support is lent to the suggestion of a sub-grain coalescence mechanism by the texture work. The small number of pole figures and their incomplete nature mean that great care must be taken in drawing conclusions from them. However, there does seem to be some evidence in the pole figures that a rolling texture was retained after reversion

and recrystallisation. Beck and Hu⁽¹¹⁶⁾ examined the microstructure of aluminium after 95% rolling and annealing. The rolling texture was similar to that found in the present case and was partially retained after recrystallisation. They concluded from the microstructural studies that the retaining of the rolling texture was a result of recrystallisation in situ (involving sub-grain coalescence), and recrystallisation with local reorientation where the orientation of the recrystallised grains was different from that of their local surroundings, but was similar to an orientation prevalent in the rolling texture as a whole. The suggestion that recrystallisation in situ played an important part in the retaining of the rolling texture supports the idea, in the present work, that a sub-grain coalescence mechanism was involved.

The recrystallisation mechanism of the retained austenite has not been investigated, but Figs. 6.16.1 and 6.16.2 do not indicate the formation of any sharp sub-grain structure. The absence of any detected sub-grain structure, together with the much faster recrystallisation of the retained austenite as compared with the reversed austenite, indicate that a different mechanism was involved, possibly the grain boundary bulge mechanism.

Consideration of the deformation characteristics of the austenite and the martensite may enhance the understanding of why different recrystallisation mechanisms were involved. The f.c.c. austenite has a low stacking fault energy and, consequently, dislocation dissociation occurs and dislocation climb is restricted. In the b.c.c martensite, however,

dislocations are able to climb more easily, and, therefore, more distinct cell structures are able to form⁽⁹⁷⁾. The facility for dislocation climb also allows more homogeneous deformation to occur. This homogeneous deformation reduces the tendency for grain boundary bulging to occur, since it reduces the difference in stored energy between neighbouring grains.

The faster recovery of the reversed austenite as compared with the retained austenite reduces the driving force for recrystallisation and, therefore, may also contribute to the reason for different recrystallisation mechanisms. The faster recovery of the reversed austenite was presumably due to a greater dislocation density and different dislocation configuration to the retained austenite.

Recrystallisation by a sub-grain coalescence mechanism must take longer, for a given driving force, than nucleation by a grain boundary bulge mechanism since, in the former case a high angle boundary has to be formed, whilst in the latter case one is already present. It should be mentioned that a high angle boundary is generally required for recrystallisation since only such a boundary has sufficient mobility to sweep through the dislocated regions⁽¹⁰³⁾. Thus, it seems that the two different recrystallisation mechanisms may be an explanation of the different rates of recrystallisation of the retained and reversed austenite. The later stages of the total recrystallisation process appear to have been a competition between the growth of the recrystallised, retained austenite into the reversed austenite regions, and the recrystallisation of the reversed austenite itself.

CHAPTER 7

PRECIPITATION IN AN FE-CR-NI-CU ALLOY

The aim of the investigation with the Fe-Cr-Ni-Cu alloy was to study the effects of precipitates other than carbides on the strength, formation, and recrystallisation of reversed austenite, and on the formation of second generation martensite. The Fe-Cr-Ni-Cu system was chosen for two main reasons:

- 1) Copper goes readily into substitutional solid solution in austenite at the solution treatment temperature of 1050°C used for alloy A. When subsequently precipitated at a lower temperature the precipitate consists of over 90% copper, thus, the matrix composition and properties are not radically altered by the precipitation.
- 2) Copper has only a moderate effect on the M_s temperature. In order to study the reverse martensite transformation it is advantageous to keep the M_s below room temperature so that room temperature measurements may be taken without the complication of the presence of second generation martensite. However, the M_s must be high enough to allow the formation of a reasonable amount of martensite on quenching to -196°C. The M_s must also be low enough so that, after precipitation, the M_s does not rise to above room temperature.

Initial experimentation with the composition of the alloy showed that copper had approximately the same effect on the M_s as nickel. Therefore the amount of nickel was lowered from its level in alloy A by the amount of copper

added. The copper was restricted to 2% so that the M_s was not raised too much by the loss of copper from solution on precipitation. 2% copper was found to dissolve readily in austenite in 20 minutes at 1050°C, as would be expected from its solubility in iron. Thus, the composition chosen was Fe - 16%Cr - 10%Ni - 2% Cu. The results, however, were disappointing due to a higher solubility of copper in austenite at the reversion temperatures and below than had been expected.

7.1 RESULTS.

7.1.1 General Properties.

The Fe - 16%Cr - 10%Ni - 2% Cu alloy was found, by quenching to various temperatures and testing magnetically, to have an M_s of $-50^{\circ}\text{C} \pm 5^{\circ}\text{C}$. Approximately 15% martensite was produced by quenching for 15 minutes at -196°C , and approximately 12% martensite was produced by 50% deformation by rolling at room temperature. The A_f was found, again magnetically, to be $660^{\circ}\text{C} \pm 5^{\circ}\text{C}$. The martensite was found to be very similar to that in alloy A in terms of hardness and microstructure, as well as in the amount produced by the various treatments.

7.1.2 Ageing.

Fig. 7.1 shows the ageing curves for various starting structures of alloy C. It was found that increases in hardness could be produced on ageing partially martensitic structures at $400-500^{\circ}\text{C}$, and 450°C was chosen as a standard ageing temperature. It can be seen in Fig. 7.1 that the two partially martensitic structures, the as quenched and cold rolled specimens containing approximately 15% and 12% martensite respectively, showed hardness peaks after ageing for 15-30 minutes at 450°C , the hardness then decreasing with increasing ageing time.

The austenitic structures, however, showed much less tendency for the hardness to increase on ageing. The solution treated structure showed no evidence at all of a hardening response on ageing. The quenched and reversed structure showed

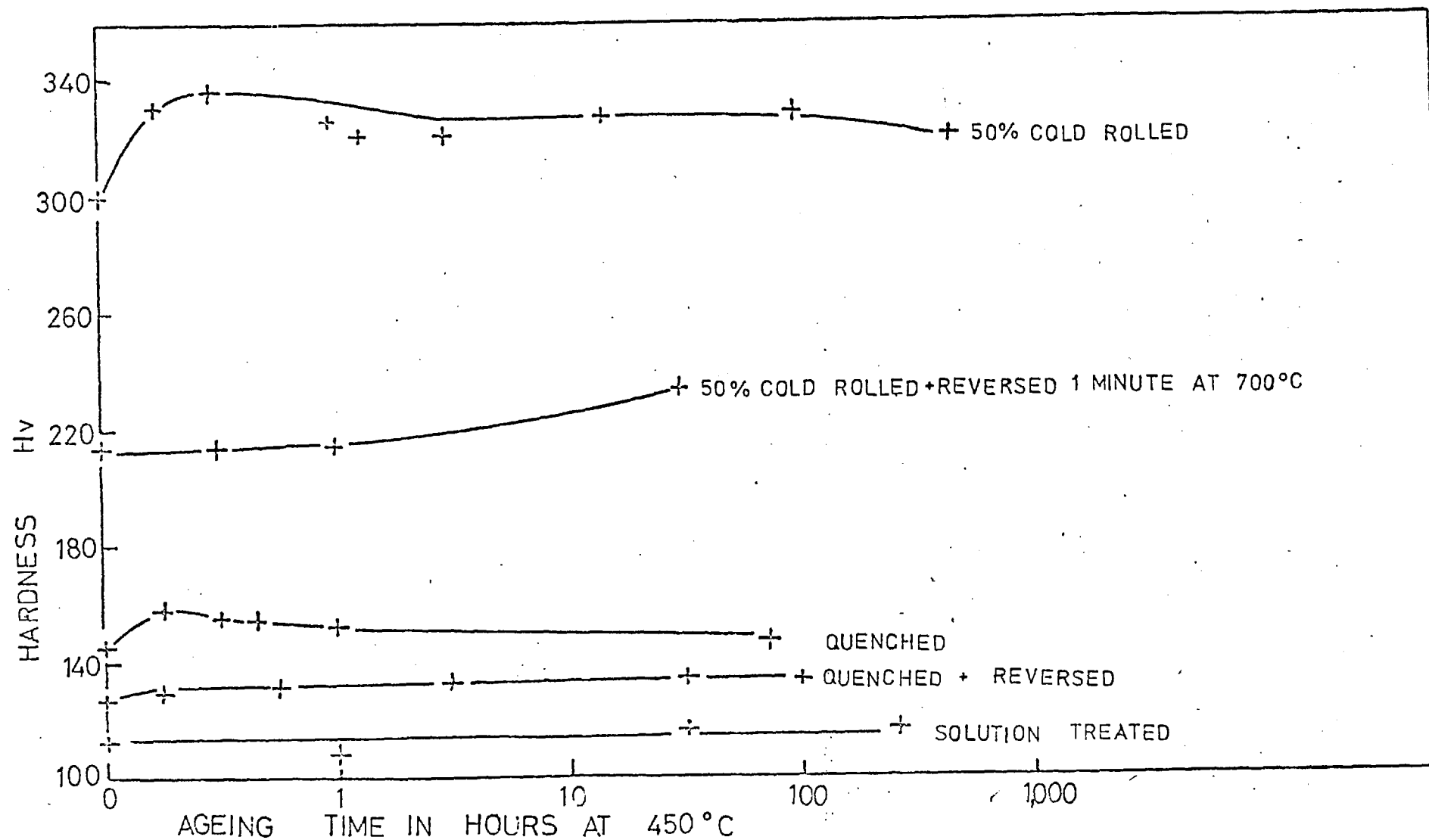


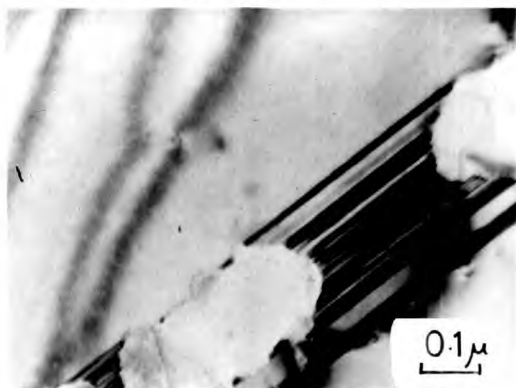
Fig. 7.1. Alloy C. Hardness changes during ageing various starting structures at 450°C.

a tendency for the hardness to increase with ageing up to 100 hours, but the effect was so small as to be inconclusive evidence of any precipitation hardening. The cold rolled and reversed specimens also showed an increase in hardness up to 100 hours ageing, the increase being somewhat larger than in the quenched and reversed specimens.

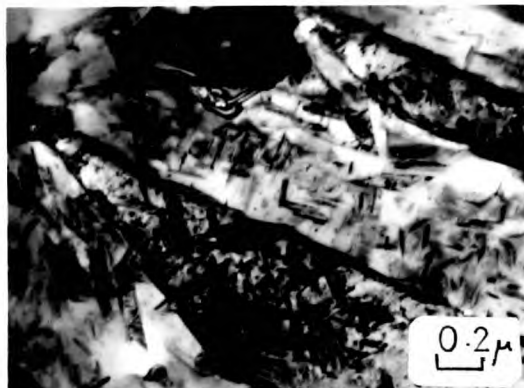
Fig. 7.2 shows some of the structures associated with the hardness results in Fig. 7.1. Fig. 7.2.1. shows a quench-induced martensite lath, after ageing to peak hardness, i.e. for 15 minutes at 450°C . Despite the high magnification of the micrograph, no precipitates were visible. The basic structure, however, was very similar to that in alloy A. After ageing quench-induced martensite in alloy C for 100 hours at 450°C , rod-shaped precipitates approximately $0.2\ \mu$ in length were visible and can be seen in Fig. 7.2.2 and in dark field in Fig. 7.2.3. Fig. 7.2.4 shows a reversed austenite lath after ageing for 100 hours at 450°C , and, once again, no precipitates were visible. No precipitation was observed in any solution treated, cold worked or cold worked and reversed specimens after any ageing treatments; in the case of the cold worked specimens, however, this may have been due to the heavy deformation structure obscuring any precipitates.

In order to establish if precipitation hardening in martensite could be transmitted to reversed austenite, specimens were taken of quenched structures aged both to peak hardness and for longer times, and reversed for one minute at 660°C . The hardness of specimens after these treatments was found to be the same as that of unaged and

Fig. 7.2



7.2.1. Alloy C. Quenched to -196°C + 15 minutes at 450°C .



7.2.2. Alloy C. Quenched to -196°C + 100 hours at 450°C .



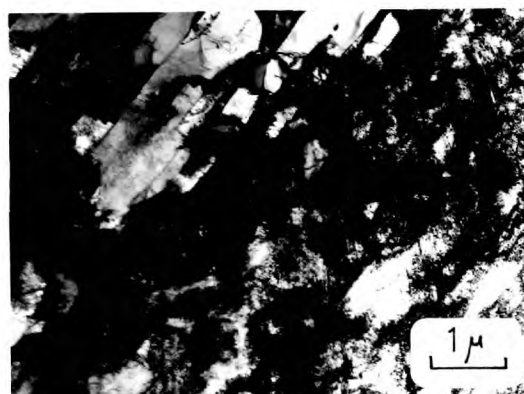
7.2.3. Alloy C. Dark field micrograph of the same region as Fig. 7.2.2. taken from a precipitate reflection



7.2.4. Alloy C. Quenched to -196°C + 1 minute at 650°C + 100 hours at 450°C .



7.2.5. Alloy C. Quenched to -196°C + 100 hours at 450°C + 1 minute at 700°C



7.2.6. Alloy C. Cold rolled 50% at room temperature + 10 hours at 450°C + 2 minutes at 700°C .

reversed specimens. Fig. 7.2.5 shows the structure of a martensite lath after ageing for 100 hours at 450°C followed by one minute at 700°C . No precipitates were visible.

An attempt was made to discover if precipitates had any effect on the recovery and recrystallisation characteristics of the austenite in alloy C. Specimens of cold rolled material were taken and some were aged to peak hardness i.e. for 30 minutes at 450°C , or for longer times. The decrease in hardness on holding both aged and unaged specimens for various times at 700°C was then determined. The results are shown in Fig. 7.3. It can be seen that the increased hardness produced by the ageing treatment had disappeared after two minutes at 700°C , and that the subsequent recovery and recrystallisation kinetics of the two sets of specimens were essentially the same. Fig. 7.2.6 shows a cold worked structure which had been aged for 10 hours at 450°C followed by two minutes at 700°C . Recovery appeared to be proceeding but no precipitates could be seen. The kinetics of recovery and recrystallisation shown in Fig. 7.3 are very similar to those shown in Fig. 6.19 for specimens of alloy A given the same rolling treatment.

The effect of precipitates on second generation martensite was briefly investigated by taking quenched and reversed specimens and ageing some for 100 hours at 450°C . Both aged and unaged specimens were then re-quenched to -196°C . No significant difference in hardness was detected between the two sets of specimens. Furthermore, no difference in hardness was detected in specimens aged after the first

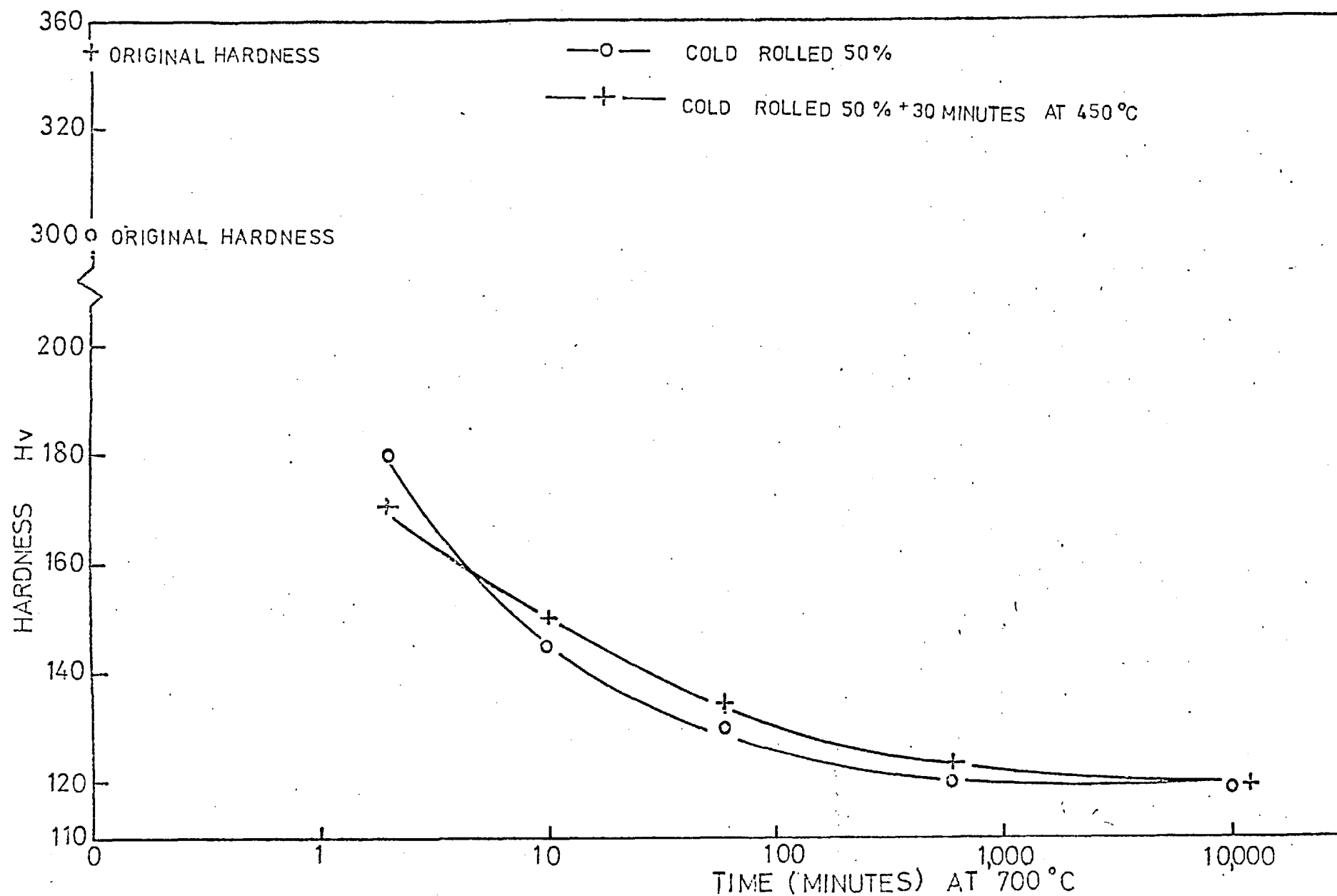


Fig. 7.3. Alloy C. Hardness changes during isothermal treatment at 700°C of aged and unaged specimens of 50% deformed material.

quench, then reversed and re-quenched. In all these cases approximately 10% martensite was produced by the second quench.

7.2 DISCUSSION

Fig. 7.1 indicates that a significant amount of precipitation occurred in martensitic structures in fairly short ageing times, but that precipitation in austenitic structures was considerably slower and occurred to a much smaller extent. There are probably several contributory factors to the difference in precipitation in martensite and austenite. Firstly, copper is considerably more soluble in austenite than in martensite at the same temperature in most iron-base alloys⁽¹²¹⁾, and, therefore, the supersaturation at ageing temperatures is greater in martensite than austenite. Secondly, the diffusion rates of solutes in b.c.c. structures in steels are generally faster than in f.c.c structures resulting in more rapid precipitation. Thirdly, the dislocation structure of both martensite and reversed austenite may have provided nucleation sites for precipitation. This third point is substantiated by the fact that the dislocation structure in reversed or deformed austenite appeared to cause some precipitation in the austenite which did not occur in the solution treated structure.

The precipitation in the martensite was not visible in the electron microscope until overageing had occurred. This is in agreement with work by Hornbogen⁽¹⁰⁵⁾ on ferritic Fe - Cu, and Speich⁽¹⁰⁶⁾ on Fe - 20 Ni - 10 Cu alloys. Both these workers suggested that peak hardness was associated with the clustering of copper atoms and it seems likely that the same was true in the present case.

Both the hardness and structural evidence points to the conclusion that any precipitates in the martensite re-dissolved very rapidly during the reverse transformation, thus making any study of the effects of these precipitates on recovery and recrystallisation impossible. The re-dissolution was presumably due to a high solubility of copper in austenite at reversion temperatures. The precipitates did not appear to affect the course of the transformation although no clear evidence was obtained on this subject except that the A_f appeared unaltered. This may suggest that the precipitates had re-dissolved before reversion was complete. Precipitation did not appear to affect the formation of second generation martensite, but the lack of clear evidence of any precipitates in the reversed austenite before the second quench makes this observation inconclusive.

The only way to have obtained clearer evidence from this type of alloy would have been to increase the copper content to, say, 4%. This, however, would have lowered the M_s to a level at which very little martensite would have been produced by quenching, or, if the other alloy content had been reduced to raise the M_s , precipitation would have resulted in the M_s rising above room temperature.

CHAPTER 8

CONCLUSIONS

The following conclusions can be drawn from observations which have been made on three alloys. Alloy A (Fe - 16Cr - 12Ni), alloy B (Fe - 15Cr - 8.5Ni - 2Mo - 0.1C) and alloy C (Fe - 16Cr - 10Ni - 2Cu):

1. On holding alloy A isothermally at temperatures between the A_S and A_F and below the A_S , martensite has been found to transform to austenite in three stages.

The first stage was temperature dependent and took place immediately the specimen attained the test temperature. This stage caused no stabilisation of the martensite and is thought to have been a martensitic reversion process similar to that described by Smith⁽¹⁾. This transformation began at 530°C and was complete at 560°C, and these were therefore taken to be the A_S and A_F temperatures. The A_S and A_F were identical for quench-induced and deformation-induced martensite.

Stage two of the transformation required an incubation period of about one minute and was both time and temperature dependent. This stage was observed between 530°C and 560°C. This is thought to have been an isothermal martensitic transformation involving the nucleation of reversed austenite in laths of martensite adjacent to laths which had already reverted during stage one.

Stage three of the transformation was found to involve the transformation of martensite to austenite over a period

of about seven days, together with the formation of a stable b.c.c. phase which would not revert martensitically to austenite even on raising the temperature to 700°C . The amount of the stable b.c.c. phase was dependent on both the temperature, and the initial martensite content. The transformation of martensite to austenite is thought to have been diffusion controlled. The stable b.c.c. phase is thought to have been a low-nickel ferrite formed either because the alloy was in the two-phase region at the temperatures involved, or due to nickel diffusion out of the martensite during the transformation causing the composition in these areas to reach that of the two-phase region. Recovery is also thought to have played a part in the stabilisation of the ferrite. Stage three was found to occur between 430°C and 560°C .

All three stages involved a decrease in hardness.

2. The long, thin twins observed after reversion by Smith⁽¹⁾, were observed below the A_s and in warm worked austenitic structures. These twins were therefore not thought to be part of the reverse martensite transformation. They may have arisen during the reversion of ϵ to austenite, or by the coalescence of high energy stacking faults present due to the reversion of ϵ or from the direct transformation.
3. The formation of some polygonised grains was observed on isothermal holding and these were thought to arise due to recovery processes.

4. The M_s was found to be considerably lower in thin foils of alloy A than in bulk material. The reason for this was probably the lack of critical nuclei in the thin foil material. Martensite was found to grow in thin foils partly by bursting and partly by slow boundary migration. The slow growth was thought to be an effect of transformation in thin foils. ϵ was not found to be an intermediate phase in the transformation to martensite, but it was observed before martensite formation and may have assisted in the nucleation of martensite. Some stacking faults in austenite were thought to be generated by the martensite transformation.
5. Second generation martensite in alloy A was thought to form in the same regions as the first generation martensite, but probably in areas which had been previously ϵ or faulted austenite rather than prior martensitic areas.
6. The presence of reversed austenite was found to stabilise austenite with respect to martensite formation. The M_s was lowered by the presence of reversed austenite but the main cause of stabilisation was thought to be the restriction on the growth of martensite laths by the defect structure of reversed austenite. Increasing the reversion temperature was found to decrease the stabilisation. The A_f was found to be unaffected by transformation cycling.
7. The presence of martensite or reversed austenite in a stainless steel has been found to increase its strength.

In alloy A, the 0.2% proof stress was found to increase linearly, and at approximately the same rate, with increasing quench-induced martensite or reversed austenite up to about 21% of each phase. The U.T.S was also found to increase linearly with martensite content, but to be virtually unaffected by reversed austenite. The ductility decreased considerably less with increasing reversed austenite than with increasing martensite.

The main strengthening mechanism in reversed austenite was thought to be the increased dislocation density as compared with annealed austenite. In the case of partially martensitic specimens the rise in U.T.S. has been explained in terms of a different work hardening mechanism as compared with reversed austenite, due to the high-angle boundaries around martensite crystals, and the different slip systems operating in martensite and austenite.

8. In alloy A 50% deformation by rolling at room temperature was found to produce 15% martensite, and 50% deformation at -78°C to produce 85% martensite. In alloy B similar deformations resulted in 40% and 90% martensite respectively. The structure of deformation-induced martensite was very similar to that of quench-induced martensite.
9. In alloy A the 0.2% proof stress and hardness increased linearly with increasing deformation-induced martensite produced by 50% deformation at various temperatures. In alloy B, however, the hardness increased with increasing deformation-induced martensite until the deformation

temperature fell below 0°C . whereupon the hardness fell suddenly and then rose again as the deformation temperature was further decreased.

The strength of deformed stainless steel has been discussed in terms of a number of contributing factors including the deformation of austenite, the formation of martensite, the deformation of martensite, strain-ageing, and the deformation temperature.

10. The reversion of deformed alloy A for two minutes at temperatures below 650°C resulted in the strength increasing with reversed austenite content up to a peak at 50% reversed austenite, and then decreasing with increasing reversed austenite content up to 85%. This decrease was thought to be due to the faster recovery of reversed austenite than retained austenite. Reversion of alloy A above 650°C resulted in recrystallisation of the deformed, retained austenite. The strength remained virtually constant with reversed austenite content up to 50% and then increased with reversed austenite content up to 85%.

The hardness of reversed, deformed alloy B followed the same trends with increasing reversed austenite as did the hardness of the ^{as}deformed material with increasing martensite content. The reversed structures in deformed alloy B were thought to have inherited the basic features of the deformed material. No recrystallisation was observed in alloy B for two minute reversion treatments up to 800°C .

11. Reversion for two minutes of deformation-induced

martensite above 700°C in both alloy A and alloy B resulted in the formation of a fine sub-grain structure within previously martensitic laths.

12. In 50% deformed alloy A, recovery and recrystallisation was thought to have occurred by a different mechanism in retained as compared with reversed austenite. Recovery is thought to have occurred faster in reversed austenite than in retained austenite due to the higher dislocation density. Recrystallisation, however, occurred faster in retained austenite than reversed austenite. The retained austenite is thought to have recrystallised by a grain-boundary bulging mechanism; whilst reversed austenite is thought to have recrystallised by sub-grain coalescence.
13. The presence of reversed, deformation-induced martensite resulted in considerable stabilisation of austenite with respect to second generation martensite formation. This stabilisation has been attributed to the defect structure of the reversed austenite.
14. Rod-shaped precipitates were observed in the martensite on ageing partially martensitic specimens of alloy C at 450°C . The age-hardening resulting from these precipitates reached a peak before the precipitates were visible in the electron microscope, and peak hardness was thought to be associated with the clustering of copper atoms. The precipitates redissolved in less than one minute on reversing the martensite to austenite at 660°C , which was the A_f

temperature. Slight age-hardening was observed on ageing reversed or cold worked austenite of alloy C at 450°C.

15. No difference in the recovery or recrystallisation characteristics at 700°C could be detected between specimens of alloy C which had been previously aged and those which had not been aged. The precipitates were thought to have re-dissolved prior to recrystallisation occurring.

SUGGESTIONS FOR FUTURE WORK.

Some possibilities for future work arise directly from the present investigation. The composition of the stable b.c.c. phase developed during isothermal holding between the A_S and A_F could probably be found much more accurately using an E.M.M.A. instrument now available in several research establishments. This knowledge would probably throw further light on the formation of this stable phase and its nature.

The direct observation of the formation of first and second generation martensite ought to be possible in improved cooling stages, particularly in the 1,000 KV. electron microscopes now available. This should shed further light on the sites of formation of second generation martensite. The advent of the 1,000 KV. electron microscope with its improved vacuum system should also enable direct observation of the reverse martensite transformation in a heating stage. This should enhance the understanding of the mechanisms of both the martensitic and isothermal reversion processes.

A more detailed study of the deformation of these stainless steels would help the understanding of the strengthening resulting from deformation. Particularly, it would be interesting to know at what stage of the deformation the martensite begins to form at various temperatures. Microhardness measurements of the hardness of martensite and austenite at various stages of deformation may also be useful.

The grain refinement produced by reversion of deformation induced martensite may be exploited in materials where toughness is a prime requirement, for example in lower alloy steels.

The study of precipitation may be extended to an alloy with 4% Copper or to other precipitates, such as Ni_3Al , Ni_3Ti , or various carbides. Maraging steels seem possible materials for the study of the combined effects of reversion and precipitation.

More generally, the amounts of martensite which can be produced in austenitic stainless steels are not high enough for the reverse martensite transformation to be potentially very useful. Other ferrous materials may utilise this transformation to produce strengthening without any external shape change. Low alloy steels, case-hardening steels and martensitic stainless steels seem possible materials for study.

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APPENDIX A.

ESTIMATION OF MARTENSITE CONTENT USING A MAGNETIC RING BALANCE

The measurements of magnetic phase content were made using a magnetic ring balance constructed in this department by H. Smith. Full details of the apparatus can be found in Smith's Ph.D thesis⁽¹⁾. The use of the ring balance was preferred to other techniques for measuring martensite content due to its relative insensitivity to factors such as grain size, internal stresses, cracks and the size distribution of the laths of martensitic phase. The contribution of austenite could be neglected as it is paramagnetic, and so the saturation magnetic intensity of the specimens gave a direct measure of the ferromagnetic martensite or ferrite content.

The magnetic balance measures the force on a ferromagnetic specimen placed in a non-uniform magnetic field with a constant field gradient produced by an electromagnet. The specimen, placed in a position of constant field gradient, experiences a force in the direction of the field gradient (i.e. vertically downwards in this case). The force on the specimen is given by $F = \sigma m \frac{dH}{dx}$ where σ is the saturation magnetic moment per unit mass or specific magnetic intensity of the specimen, m is the mass of the specimen, and $\frac{dH}{dx}$ is the field gradient. This force produces a downward displacement, D , which is balanced by the elastic distortion of the ring from which the specimen is suspended. Therefore, $D \propto F$. Thus, $D = K m \sigma$, where K is a constant for the apparatus.

The apparatus is calibrated using a pure iron specimen of known mass. Hence
$$\frac{D_s}{D_{Fe}} = \frac{m_s \cdot \sigma_s}{m_{Fe} \cdot \sigma_{Fe}}$$

where s signifies the test specimen, and Fe the pure iron specimen. If the specimen contains only one ferromagnetic phase, M, then $\sigma_s = \sigma_M \cdot \%M/100$.

Thus,

$$\frac{D_s}{D_{Fe}} = \frac{m_s \cdot \sigma_M \cdot \%M}{m_{Fe} \cdot \sigma_{Fe} \cdot 100}.$$

Thus, if D_s , D_{Fe} , m_s and m_{Fe} are measured, and σ_M and σ_{Fe} are calculated, $\%M$ can be deduced.

σ_M was calculated for each alloy taking into account the effects of the various alloying additions on σ_{Fe} . Particularly, chromium, nickel and copper atoms substituted in the iron lattice were allowed for in the calculation.

The balance was calibrated and its performance assessed by experiments based on those of Glover (Ph.D thesis, University of Birmingham, 1956). The sensitivity of the apparatus depends on two factors; firstly, on the stability of the field current and secondly, on the accuracy of the measurement of specimen displacement. In the current apparatus these allowed 0.1% martensite to be detected. The error at levels of martensite less than 10% was about 0.05% martensite, and at higher levels of martensite it was about 0.2% martensite.

The reproducibility was found to be such that, in 50 measurements, a scatter of 0.1% martensite was found at the 10% martensite level.

The absolute accuracy of the apparatus was not assessed by direct calibration with X-ray or other techniques, however, it is dependent on the accuracy of the calculated σ_M values. If

the error in σ_M were as high as 10 in the values of about 170, this would correspond to an error of 0.6% martensite at the 10% martensite level. The error in σ_M is, however, unlikely to have been this great.

APPENDIX B.DILATOMETRY MEASUREMENTS

The dilatometry measurements were made on an apparatus constructed in this Department by Mr. F. A. Thompson and described in detail by Barford (J. Sci. INSTRUM., 1963 VOL 40, p.001). The differential technique, using a control specimen of the same coefficient of thermal expansion as the real specimen, is necessary since the value of the thermal expansion up to the temperature range required is large compared to the dilation on transformation. For example, on heating from room temperature to 700°C a stainless steel specimen 4 cm. long undergoes a thermal expansion of about 450 microns whereas the contraction due to a martensite content of about 15% transforming to austenite in such a specimen is found to be of the order of 40 microns.

Length changes are measured using a variable inductance transducer. Thermal expansion of the control specimen during heating acts to move the body of the transducer; thus although the real specimen also expands on heating and moves the transducer operating pin, only changes in length due to transformations are recorded by the transducer. However, this is not strictly true for the present series of measurements since the control specimen has an f.c.c. austenitic structure whereas the real specimens contain various amounts of b.c.c. martensite (and possibly h.c.p. martensite). The b.c.c. structure has a lower coefficient of thermal expansion than the f.c.c. so an apparent specimen contraction is indicated as the temperature is raised.

Any small difference in length between the real and control specimens will produce a change in the transducer readings with temperature, of a magnitude and direction which will be dependent on the relative lengths of the specimens; it may tend either to reinforce or counteract the effect due to the different crystal structures. The present investigation is concerned more with the temperatures at which non-linear length changes due to phase transformations occur, than with the absolute values of the magnitudes of such changes. These two effects were, therefore, unimportant.

However, of far greater importance is the possibility that the temperature of the two specimens increased at different rates due to differences in their surface condition (i.e. different reflectivities and emissivities). Before each run both specimens were chemically cleaned and then rubbed with fine silicon carbide paper so that their surface conditions were identical. As the surface effects were likely to influence the results during the initial rapid rise in specimen temperatures, results obtained below 300°C were not used.

Specimens were 4 cm. in length by 1 cm. wide and 0.020" in thickness; the length of the furnace constant temperature zone together with the small specimen thickness ensured that both longitudinal and transverse gradients within the specimens were minimised. The specimen temperature is measured by a thermocouple mounted with its end close to the specimen.

The reproducibility of the results was considered to be very good in that repeated runs on similar specimens gave curves of the same form and the temperatures at which abrupt changes occurred agreed to within 5°C even with the fastest heating rate.